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## THE RELATION BETWEEN CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES IN THE GARNET GROUP

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In 1915, W. E. Ford<sup>1</sup> showed that the optical and physical properties of a garnet were directly dependent on its chemical composition, so that its refractive index and specific gravity could be calculated quite accurately from the chemical analysis. In the period of twenty-one years since Ford's paper was published, a great many analyses of the garnets have appeared, and the optical and physical properties of many of those analyzed have been determined. As these analyses had been compiled and studied in the course of the revision of the sixth edition of Dana's System of Mineralogy, it seemed worthwhile to bring Ford's work up to date.

It should be pointed out that Ford's calculations were based on the assumption that all garnets conformed to the ideal group formula,  $3\text{RO} \cdot \text{R}_2\text{O}_3 \cdot 3\text{SiO}_2$ , the analyses studied being recalculated to fit this ideal formula. In recent years, however, x-ray work has led to the belief that isomorphous replacement in a mineral group need not be restricted to atoms of the same valence, an outstanding example being the replacement of Si by Al in the amphiboles.<sup>2</sup> If such replacements occur in the garnet group, Ford's method of calculating compositions would be open to serious objection.

This objection has recently been raised by Alderman,<sup>3</sup> who analyzed a garnet, very nearly pure almandite, and found that the analysis showed considerable deviations from the ideal garnet formula, the molecular ratio obtained being 2.91:1.06:2.92 instead of 3:1:3. Alderman cites several other analyses whose molecular ratios deviate considerably from the ideal. He believes that in these cases, Al replaces both Si and ferrous iron. While such replacements appear possible from a consideration of the atomic radii, there are no theoretical grounds on which to decide whether or not they might be expected to occur in any

<sup>1</sup> Ford, W. E., *Am. J. Sci.*, vol. 40, p. 33, 1915.

<sup>2</sup> Cf. Warren, *Zeits. Krist.*, vol. 72, p. 493, 1930.

<sup>3</sup> Alderman, *Min. Mag.*, vol. 23, p. 42, 1935.

particular mineral. However, a study of the analyses in the literature should shed some light on the frequency and extent of such replacements.

Such a study shows that most of the garnets analyzed conform very closely to the ideal ratio, and that those which do not, including those cited by Alderman, show only limited deviations. Furthermore, with few exceptions, those showing noticeable deviations fall into two groups: garnets containing an appreciable amount of  $\text{TiO}_2$ , and garnets rich in  $\text{FeO}$ . There is considerable uncertainty at present as to the rôle of titanium in garnets. The problem has been discussed by Kunitz,<sup>4</sup> who came to the conclusion that Ti replaces Si in these garnets. In nearly all the recent analyses, however, the molecular ratios are high for  $\text{RO}_2$  and  $\text{RO}$ , and low for  $\text{R}_2\text{O}_3$ , which makes plausible the suggestion of Zedlitz<sup>5</sup> that part of the titanium is present in the trivalent state. (Any  $\text{Ti}_2\text{O}_3$  present would cause a corresponding amount of  $\text{Fe}_2\text{O}_3$  to be reported as  $\text{FeO}$ .) In view of this uncertainty, the titaniferous garnets have been excluded from the following discussion.

With only a very few exceptions, the garnets of the second group deviate from the ideal group formula in the same way. All give molecular ratios high in  $\text{R}_2\text{O}_3$  and low in  $\text{RO}$ . Every one of the analyses cited by Alderman falls into this group. While this might be taken, following Alderman, to indicate that Al replaces Si and ferrous iron, there is an alternative explanation. It is well known that the accurate determination of ferrous iron in a refractory mineral is extremely difficult.<sup>6</sup> The analysis of an almandite garnet for  $\text{FeO}$  is very likely to give a low result because of incomplete solution of the mineral or partial oxidation during the necessary preliminary grinding. Thus part of the  $\text{FeO}$  is likely to be reported as  $\text{Fe}_2\text{O}_3$ . Without denying the possibility that replacements such as those suggested by Alderman may occur in the garnet group, it seems more plausible to ascribe the reported deviations from the ideal group formula to analytical error, particularly in the  $\text{FeO}$  determination.

It would seem, therefore, that the method of calculation used by Ford is justified. It has been used in the present work, with two modifications. For reasons stated above, the titaniferous garnets have been omitted. However, since so many analyses give small amounts of  $\text{TiO}_2$ , the upper limit allowed has been somewhat arbitrarily set at 0.50%  $\text{TiO}_2$ , and these small amounts have been calculated as  $\text{SiO}_2$ . No correction has been applied for the  $\text{TiO}_2$  present, but the error thus introduced is apparently

<sup>4</sup> Kunitz, *Neues Jahrb. Min., Geol., Beil.-Bd.*, 70A, p. 395, 1936.

<sup>5</sup> Zedlitz, *Zentrabl. Min.*, 1935A, p. 68.

<sup>6</sup> Cf. Hillebrand and Lundell, *Applied Inorganic Analysis*. John Wiley and Sons, New York, 1929, pp. 769-785.



small. There are as yet insufficient data to evaluate accurately the effect of  $\text{TiO}_2$  on refractive index and specific gravity in the garnets, but to judge from the data given by Kunitz,<sup>4</sup> the presence of 0.50%  $\text{TiO}_2$  in andradite garnets raises the refractive index approximately 0.004 and the specific gravity approximately 0.005.

The second modification in the calculations was used for analyses high in FeO, with ratios deviating from the ideal. In line with the reasoning given above, sufficient of the  $\text{Fe}_2\text{O}_3$  reported in the analysis was calculated to FeO to correct the molecular ratio to 3:1:3. This has the effect of increasing the calculated almandite and grossularite content while decreasing the andradite content. In most cases, the values calculated for refractive index and specific gravity are changed only slightly by this procedure, owing to the fact that the changes are nearly compensatory in effect.

Table 1 below gives a summary of 57 analyses published since 1915 with the calculated compositions and the observed and calculated refractive indices. The values used for the component molecules were those given by Ford:—Pyrope (Py) 1.705, grossularite (Gr) 1.735, spessartite (Sp) 1.800, almandite (Al) 1.830, uvarovite (Uv) 1.870, andradite (An) 1.895. It is apparent that there is excellent agreement between the observed and calculated values, the results in Table 1 furnishing a striking confirmation of Ford's values for the refractive indices of the component garnet molecules. For all 57 analyses, the average difference between observed and calculated refractive indices, disregarding plus and minus signs, is 0.006. In seven cases, Nos. 13, 23, 35, 52, 54, 56, and 57, the difference is greater than 0.010. If these are omitted, the average difference for the remaining fifty analyses is 0.0035, and the algebraic sum of the differences is very nearly zero.

Of these seven analyses, No. 13 is particularly interesting, because its composition is unique. The grossularite-andradite garnets have generally been considered to be only partly miscible with the almandite-spessartite-pyrope garnets, the limit of miscibility usually being placed at 20–30% Gr-An (cf. the diagrams given by Ford). This garnet lies far outside this range. Heritsch makes the interesting suggestion that it may be a double salt like dolomite. If this were the case, it might explain the difference between the observed and calculated values of the refractive index. It should be noted, however, that the unit cell calculated for this garnet by the additive rule agrees very closely with that observed by Heritsch (see No. 4 of Table 2).

TABLE 1. CALCULATED AND OBSERVED REFRACTIVE INDICES, AND COMPOSITIONS OF 57 GARNETS

	Gr	An	Al	Py	Sp	Uv	<i>n</i> calcd.	<i>n</i> obsd.	Diff.
1.	96.60	—	2.06	1.02	0.32	—	1.737	1.734	+ .003
2.	96.75	2.27	0.59	—	—	0.39	1.740	1.737	+ .003
3.	83.96	10.80	3.63	0.72	0.89	—	1.756	1.748	+ .008
4.	87.88	2.03	8.07	1.31	0.71	—	1.745	1.750	— .005
5.	10.31	1.26	27.31	59.83	0.68	0.61	1.746	1.750	— .004
6.	87.29	12.71	—	—	—	—	1.755	1.750	+ .005
7.	85.21	12.88	0.52	1.07	0.32	—	1.756	1.752	+ .004
8.	80.85	7.88	3.82	7.32	0.14	—	1.749	1.756	— .007
9.	18.74	2.94	28.89	48.72	0.72	—	1.753	1.756	— .003
10.	—	5.75	41.66	52.24	0.35	—	1.767	1.758	+ .009
11.	15.17	3.33	36.53	43.78	1.19	—	1.763	1.766	— .003
12.	8.43	5.93	40.98	43.16	1.50	—	1.771	1.766	+ .005
13.	35.19	11.24	45.13	7.51	0.92	—	1.794	1.777	+ .017
14.	14.17	—	55.35	27.44	3.04	—	1.781	1.782	— .001
15.	24.50	—	54.87	18.05	2.58	—	1.783	1.785	— .002
16.	12.07	—	61.08	25.13	1.72	—	1.786	1.786	.000
17.*	27.29	6.77	50.32	15.53	0.10	—	1.789	1.787	+ .002
18.	26.28	6.46	49.12	13.99	4.15	—	1.791	1.787	+ .004
19.	7.86	6.22	52.46	32.07	1.39	—	1.786	1.789	— .003
20.	19.58	5.18	57.56	16.09	1.60	—	1.794	1.791	+ .003
21.	23.96	1.50	54.17	15.29	5.09	—	1.788	1.792	— .004
22.	9.16	2.61	41.12	6.95	40.16	—	1.802	1.794	+ .008
23.	1.36	3.26	10.68	0.85	83.85	—	1.805	1.794	+ .011
24.	5.07	—	4.14	1.02	89.77	—	1.797	1.796	+ .001
25.	16.44	—	63.99	15.69	3.88	—	1.794	1.797	— .003
26.	22.89	1.22	56.51	1.61	17.76	—	1.802	1.797	+ .005
27.	6.95	10.76	61.10	19.80	1.39	—	1.805	1.797	+ .008
28.	1.30	1.07	6.53	1.98	89.12	—	1.800	1.800	.000
29.*	—	2.11	73.20	20.37	4.32	—	1.805	1.804	+ .001
30.	3.07	0.89	16.89	2.23	76.92	—	1.802	1.805	— .003
31.	5.54	—	32.86	—	61.60	—	1.806	1.805	+ .001
32.*	—	2.11	74.89	17.50	5.41	—	1.808	1.806	+ .002
33.	10.61	—	73.74	11.03	4.62	—	1.805	1.808	— .003
34.*	6.70	—	52.57	1.91	38.82	—	1.810	1.808	+ .002
35.	5.05	—	90.43	2.85	1.67	—	1.821	1.808	+ .013
36.*	8.64	—	73.21	10.04	8.11	—	1.807	1.810	— .003
37.	0.67	—	33.84	1.20	64.29	—	1.809	1.811	— .002
38.*	—	5.42	37.86	—	56.72	—	1.816	1.812	+ .004
39.	1.26	2.29	15.15	2.03	79.26	—	1.804	1.813	— .009
40.	—	0.82	29.24	0.59	69.35	—	1.809	1.813	— .004
41.*	—	2.88	77.36	14.25	5.51	—	1.812	1.813	— .001
42.*	0.82	—	45.44	1.21	52.54	—	1.812	1.814	— .002
43.*	2.08	—	57.42	3.02	37.48	—	1.813	1.815	— .002
44.	2.74	2.51	83.82	3.50	7.42	—	1.822	1.816	+ .006



TABLE 1 (Continued)

	Gr	An	Al	Py	Sp	Uv	<sup>n</sup> calcd.	<sup>n</sup> obsd.	Diff.
45.*	—	1.39	36.58	3.36	58.67	—	1.809	1.817	-.008
46.*	0.74	—	74.08	5.21	19.97	—	1.817	1.817	.000
47.	—	—	62.98	4.19	32.83	—	1.815	1.818	-.003
48.*	1.01	—	74.12	4.97	19.89	—	1.817	1.818	-.001
49.	—	4.52	74.84	3.89	16.76	—	1.823	1.818	+.005
50.*	0.89	—	85.84	8.76	4.51	—	1.817	1.819	-.002
51.	—	1.48	75.00	7.90	15.63	—	1.816	1.821	-.005
52.	5.20	7.52	—	0.17	0.07	87.04	1.864	1.847	+.017
53.	7.32	1.27	—	2.05	—	89.37	1.857	1.855	+.002
54.	17.05	73.70	7.19	—	2.06	—	1.861	1.88	-.02
55.	—	95.23	1.36	3.36	0.05	—	1.888	1.887	+.001
56.	12.78	68.05	—	5.30	13.87	—	1.851	1.89	-.04
57.	2.56	92.25	—	2.49	2.69	—	1.884	1.92	-.04

Analyses marked\* are those in which some  $\text{Fe}_2\text{O}_3$  has been calculated as  $\text{FeO}$ . 1. Graham and Poitevin, *Mus. Bull. Geol. Surv. Canada*, 1918, No. 27, p. 45; from Black Lake area, Quebec, G. 3.60. 2. Herdsman quoted by Pabst, *Am. Mineral.*, vol. 21, p. 9, 1936; from Georgetown, California, G. 3.506. 3. Agar and Krieger, *Am. J. Sci.*, vol. 24, p. 77, 1932; from West Redding, Conn., G. 3.62. 4. Hezner quoted by Grubenmann (*Festschrift Dozenten Univ. Zurich*, 1914), *Neues Jahrb. Min. Geol.*, 1916, Bd. I, p. 295; from Maigelsstal, Switzerland, G. 3.611. 5. Eskola, *Vid. Skrifter, Mat.-Nat. Klasse*, 1921, No. 8, p. 27; from Rodhaugen, Sondmore, Norway, G. 3.782. 6. Eakins quoted by Cross and Shannon, *Proc. U. S. Nat. Mus.*, vol. 71, art. 18, 1927; from Italian Mt., Gunnison Co., Colorado, G. 3.629. 7. McConnell, *Am. Mineral.*, vol. 18, p. 25, 1933; from Sierra Tlayacac, Mexico, G. 3.567. 8. Bendig quoted by Gottfried, *Chem. Erde*, vol. 5, p. 106, 1930; from Passa del Termine, Adamello, Italy, G. 3.512. 9. Bennett quoted by Tilley, *Min. Mag.*, vol. 24, p. 422, 1936; from Weissenstein, Fichtelgebirge, Bavaria, G. 3.760. 10. Cornelius and Dittler, *Neues Jahrb. Min. Geol., Beil.-Bd.*, 59A, p. 53, 1929; from Val Codera, Sondrio, Italy, G. 3.84. 11. Eskola, *op. cit.*; from near Aurlandsfjord, Norway, G. 3.83. 12. Eskola, *op. cit.*; from Silden, Nordfjord, Norway, G. 3.882. 13. Heritsch, *Zeits. Krist.*, vol. 86, p. 253, 1933; from the Lieserschluht near Spittal, Carinthia, G. 3.877. 14.-16. Eskola, *op. cit.*; 14. from Tvedestrand, Norway, G. 4.02. 15. from Susselbakke, Mysen, Norway, G. 3.94. 16. from Haugen, Bamle, Norway, G. 3.984. 17. Pabst, *Am. Mineral.*, vol. 16, p. 327, 1931; from Russian River, Cal., G. 3.821. 18. Novacek (*Vestník Kral. Ces. Spol. Nauk*, 1931), *Neues Jahrb. Min. Geol.*, 1934, Bd. I, p. 363; from Ronov, Czechoslovakia, G. 3.980. 19. Thomassen quoted by Eskola, *op. cit.*; from Aardal, Sogn, Norway, G. 3.917. 20. Thomassen quoted by Eskola, *op. cit.*; from Vanelvsdalen, Sondmore, Norway, G. 3.995. 21. Novacek, *op. cit.*; from Ronov, G. 3.981. 22. Fairchild quoted by Ross, *U.S.G.S. Prof. Paper* 179, p. 63; from Ducktown, Tenn. 23. Shannon, *J. Wash. Acad. Sci.*, vol. 17, p. 444, 1927; from Amelia, Va., G. 4.153. 24. Shannon quoted by Ross and Kerr, *Am. Mineral.*, vol. 17, p. 16, 1932; from Bald Knob, N. C. 25. Eskola, *op. cit.*; from Taatø near Kragerø, Norway, G. 4.00. 26. Fairchild quoted by Ross, *op. cit.*; from Ore Knob, N. C. 27. Eskola, *op. cit.*; from Romsdalshorn, Norway, G. 3.97. 28. Otto, *Min. petr. Mitt.*, vol. 47, p. 99, 1935; from Amelia, G. 4.253. 29.-30. Novacek, *op. cit.*; 29. from Krizova hora, Czechoslovakia, G. 4.153. 30. from Budislav, Czechoslovakia, G. 4.181. 31. Strock, *Am. Mineral.*, vol. 15, p. 40, 1930; from Avondale, Pa., G. 4.117. 32. Novacek, *op. cit.*; from Krizova hora, G. 4.164. 33. Blix quoted by Du Rietz, *Geol. För. Förh.*, vol. 57, p. 190, 1935; from Muruhatten, Sweden, G. 4.145. 34. Shannon and Gonyer, *J. Wash. Acad. Sci.*, vol. 17, p. 534, 1927; from Gwynns Falls, Md. 35. Alderman, *Min. Mag.*, vol. 23, p. 42, 1935; from Botalack, Cornwall, England, G. 4.22. 36. Novacek, *op. cit.*; from Tabor, Czechoslovakia, G. 4.116. 37. Haschka quoted by Novacek, *op. cit.*; from Susice, Czechoslovakia, G. 4.168. 38. Kokta quoted by Novacek, *op. cit.*; from Drahonin, Moravia, G. 4.229. 39. Shannon

*Am. Mineral.*, vol. 11, p. 35, 1926; from Montgomery Co., Md. 40. Novacek, *op. cit.*; from Puklice near Jihlava, Czechoslovakia, G. 4.211. 41. Burri and Parga-Pondal, *Schweiz Min. petr. Mitt.*, vol. 16, p. 226, 1936; from Hoyazo, prov. Almeria, Spain, G. 4.201. 42.-43. Novacek, *op. cit.*; 42. from Zoptau, Moravia, G. 4.232. 43. from Hoslau-Nacetin, Czechoslovakia, G. 4.240. 44. Bendig quoted by Gottfried (*Sitzber. Heidelberg Akad. Wiss.* 1930), *Fortschr. Min.*, vol. 18, p. 174, 1934; from Adamello, Italy, G. 4.152. 45.-46. Novacek, *op. cit.*; 45. from near Marsikov, Moravia, G. 4.219. 46. from Svatava near Cernovice, Czechoslovakia, G. 4.249. 47. Shannon, *Am. Mineral.*, vol. 7, p. 171, 1922; from Avon Idaho. 48. Novacek, *op. cit.*; from Krizova hora, G. 4.253. 49. Bendig quoted by Gottfried, *op. cit.* #44; from Adamello, Italy, G. 4.006. 50.-51. Novacek, *op. cit.*; 50. from Kladno, Czechoslovakia, G. 4.233. 51. from Pribyslavice near Caslav, Czechoslovakia, G. 4.246. 52. Lokka quoted by Eskola, (*C. R. Soc. Geol. Finlande*, No. 7, p. 26, 1933), *Min. Abs.*, vol. 6, p. 46, 1933; from Outokompu, Finland, G. 3.75. 53. Borgström, (*Geol. För. Förh.*, vol. 23, 569, 1902), *Zeits. Krist.*, 37, 284, 1903; from Kuusjärvi, Finland, G. 3.772. 54. Kunitz, *Neues Jahrb. Min. Geol., Beil.-Bd.*, 70A, p. 395, 1936; from Risör, G. 3.762. 55. Sanero (*Per. Min. Roma*, vol. 6, p. 213, 1935), *Neues Jahrb. Min. Geol.*, 1936, Bd. I, p. 155; from Val d'Aosta, Italy, G. 3.826. 56.-57. Jenkins and Bauer quoted by Palache, *U.S.G.S. Prof. Paper* 180, 1936; from Franklin, N. J.

In all, eighty-five analyses were found, published since 1915 and accompanied by specific gravity determinations. The differences between calculated and observed values were greater than 0.1 in nine cases, the observed values being low in each case. For the remaining seventy-six, the average difference between calculated and observed values was 0.026, disregarding plus and minus signs, and the algebraic sum of the differences was practically zero. The values used for the garnet molecules were:—Pyrope 3.510, grossularite 3.530, spessartite 4.180, almandite 4.325, andradite 3.835 and uvarovite 3.775. The first three of these are identical with the specific gravities given by Ford, but those given here for almandite and andradite are somewhat higher. The recent determinations on garnets high in almandite and andradite agree very well with the new values. The specific gravity of the uvarovite molecule was calculated from two analyses only (Nos. 52 and 53 of Table 1).

As a check, the specific gravities of the garnets were also calculated from the x-ray data in the literature through the relation

$$G = \frac{Z \times \text{mol. wt.} \times 1.65 \times 10^{-24}}{a_0^3}$$

where  $Z$ , the number of molecules in the unit cell, is eight for the garnets. Table 2 gives the compositions and the observed and calculated unit cells for nineteen garnets. A large number of x-ray determinations by Stockwell and some by Menzer have been omitted because the sample used for x-ray study was not analyzed. It is well known that even garnets from the same locality may vary considerably in composition. However, Nos. 18 and 19 of Table 2 were included although the analyses were not made on the material that was used for x-ray study, because they are close to pure andradite and pyrope, respectively, and because the analyses of garnets from these localities show little variation.



TABLE 2. CALCULATED AND OBSERVED UNIT CELLS, AND COMPOSITIONS

	Gr	An	Al	Sp	Py	$a_0$ obsd.	$a_0$ calcd.	Diff.
1.	1.40	—	12.89	85.71	—	11.562	11.581	+ .019
2.	5.60	—	84.88	—	9.53	11.506	11.510	+ .004
3.	—	85.63	8.78	1.30	4.29	11.932	11.965	+ .033
4.	35.19	11.24	45.13	0.92	7.51	11.668	11.675	+ .007
5.	89.29	6.86	0.55	0.24	3.05	11.840	11.839	— .001
6.	—	1.18	81.50	1.95	15.37	11.497	11.495	— .002
7.*	—	2.75	79.83	15.76	1.66	11.521	11.524	+ .003
8.	3.70	1.66	1.54	92.27	0.83	11.603	11.604	+ .001
9.*	27.29	6.77	50.32	0.10	15.53	11.58	11.618	+ .04
10.	—	0.82	29.24	69.35	0.59	11.627	11.565	— .062
11.	—	1.48	75.00	15.63	7.90	11.579	11.515	— .064
12.*	0.74	—	74.08	19.97	5.21	11.552	11.514	— .038
13.*	1.01	—	74.12	19.89	4.97	11.606	11.515	— .091
14.*	—	2.11	74.98	5.41	17.50	11.550	11.502	— .048
15.*	—	2.11	73.20	4.32	20.37	11.569	11.500	— .069
16.	23.96	1.50	54.17	5.09	15.29	11.622	11.584	— .038
17.*	0.89	—	85.84	4.51	8.76	11.535	11.498	— .037
18.	0.73	96.91	1.60	0.07	0.69	12.030	12.030	.000
19.	0.62	4.67	14.67	0.25	74.28			
			Uv 5.52			11.510	11.513	+ .003

Analyses marked \* are those in which some  $\text{Fe}_2\text{O}_3$  has been calculated as  $\text{FeO}$ .

Accuracy of observed  $a_0$  stated to be  $\pm 0.01$  or better, except for No. 9 which is given  $\pm 0.03$ , and Nos. 10–17, for which the probable error is not stated. 1.–2. Stockwell, *Am. Mineral.*, vol. 12, p. 327, 1927; Nos. 9 and 20; 1. on same material as analyzed by Penfield, *Dana's System*, 6th Ed., p. 442; from Branchville, Conn. 2. on same material as analyzed by Sperry quoted by Ford, *op. cit.*, from Redding, Conn. 3. Zedlitz, *Zentralbl. Min.*, 1933A, p. 225; analysis of somewhat impure material by Machatschki and Weinzödl, from Mixnitz, Styria. 4. Heritsch, *Zeits. Krist.*, vol. 86, p. 253, 1933; from the Lieserschlucht near Spittal, Carinthia. 5.–8. Menzer, *Zeits. Krist.*, vol. 69, p. 369, 1928; 5. from Xalostoc, Mexico, 6. from Falun, Sweden, 7. from Engasö, Sweden, 8. from Tsilaisina, Madagascar. 9. Pabst, *Am. Mineral.*, vol. 16, p. 327, 1931; from Russian River, Cal. 10.–17. Novacek (*Vestník Kral. Ces. Spol. Nauk*, 1931), *Neues Jahrb. Min. Geol.*, 1934, Bd. I, p. 363; from Czechoslovakian localities. 18. Menzer, *op. cit.*; composition from an analysis by Scherf quoted by Rakusz, *Zentralbl. Min.*, 1924, p. 353; from Dobschau. 19. Menzer, *op. cit.*, composition from analyses by v. John, *Jahrb. k.k. geol. Reichsanst.*, vol. 42, p. 53, 1892, and Seebach, *Zentralbl. Min.*, 1906, p. 772; from Meronitz, Bohemia.

The values of  $a_0$  for the garnet molecules which were used to obtain the calculated unit cells in Table 2 are given below in Table 3. Those given by Stockwell<sup>7</sup> are included for comparison. The differences are slight, since both sets of values are based primarily on the work of Menzer and of Stockwell. Examination of Table 2 shows that there is good agreement between calculated and observed values of  $a_0$  except for the eight determinations by Novacek. These are believed to be in error. When the calculation above is reversed, and specific gravities

<sup>7</sup> Stockwell, *Am. Mineral.*, vol. 12, p. 327, 1927.

are calculated from his analyses and his values for  $a_0$ , the values calculated for specific gravity are considerably lower than those he observed, indicating that his values for  $a_0$  are too high.

The specific gravities calculated from  $a_0$  by the relation given above are listed in Table 3. Comparison with those derived from the specific gravity data in the literature shows that the agreement is excellent for almandite and andradite, fairly good for spessartite, and rather poor for grossularite and pyrope. Those calculated from the  $x$ -ray data are higher. The discrepancy may be due to errors in the specific gravity determinations, which tend to be too low, but further  $x$ -ray work on analyzed garnets is needed.

TABLE 3. UNIT CELLS AND SPECIFIC GRAVITIES OF THE GARNET MOLECULES

	$a_0$	$a_0$ Stockwell	Mol. Wt.	G. calcd. from $a_0$	G. from sp. gr. data
Grossularite	11.840	11.840	450.4	3.582	3.530
Andradite	12.045	12.040	508.1	3.838	3.835
Uvarovite	12.05*	—	500.2	—	3.775
Almandite	11.495	11.493	497.6	4.325	4.325
Spessartite	11.590	11.577	494.9	4.196	4.180
Pyrope	11.440	11.430	403.1	3.554	3.510

\* Calculated from specific gravity = 3.775.

A number of different physical properties of the garnets have been suggested as the basis of determinations of the chemical compositions without analysis. Since  $x$ -ray patterns cannot usually be made, refractive index and specific gravity are the properties most helpful and easiest measured. Philipsborn<sup>8</sup> gives tetrahedral diagrams in which refractive indices and specific gravities are plotted. However, these are rather inconvenient to use, and do not give a corresponding gain in accuracy. The three-component diagrams given by Ford appear to be the most suitable for every-day use. The helpful table prepared by Heritsch,<sup>9</sup> showing the range of composition of garnets from various rock types, may be used as a guide in the determination. Occasionally, a qualitative test for manganese is a necessary supplement. Trials with Ford's diagrams, redrawn using the new values for the specific gravities of almandite and andradite, gave the following results: The agreement between deduced and actual compositions was excellent for the garnets from limestone contact zones (largely grossularite-andradite), but was

<sup>8</sup> Philipsborn, *Sächs. Akad. Wiss., Mat.-Phys. Klasse*, vol. 40, p. 34, 1928.

<sup>9</sup> Heritsch, *Neues Jahrb. Min., Geol., Beil.-Bd.*, 55A, p. 74, 1926.



only fair for the garnets from pegmatites (largely almandite-spessartite), because the refractive indices and specific gravities of almandite and spessartite are so little different. This method of determination is unsatisfactory for garnets from schists and eclogites because these garnets usually contain four components (almandite, pyrope, grossularite, andradite) in significant amounts. However, the use of either of the three-component diagrams almandite-pyrope-grossularite or almandite-pyrope-andradite will give a good approximation of the almandite content, though giving no accurate idea of the amounts of the other components.

#### ACKNOWLEDGMENT

The writer thanks Professor W. E. Ford of Yale University and Dr. Earl Ingerson of the Geophysical Laboratory of the Carnegie Institution of Washington for friendly advice and criticism.

#### SUMMARY

Examination of the garnet analyses published in 1915 has verified the direct relationship between chemical composition and physical properties found by Ford to exist in the garnet group. The refractive indices, specific gravities and sizes of unit cells have been calculated for the different garnet molecules.

# ACCURATE ORIENTATION OF THIN SECTIONS\*

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## INTRODUCTION

With the advent of petrofabric analysis has come the necessity for accurate measurement and recording of the orientations of thin sections with respect to geographic directions, or structures in the rocks, or both. Oriented sections have been used in Europe extensively since 1925, and are being more and more used in America, but, as far as the writer is aware, there is no apparatus in use for determining orientation accurately. It is commonly approximated by using combinations of protractor, straight edges, and reference lines on paper or cardboard. Such crude methods often give errors of  $10^{\circ}$  to  $15^{\circ}$  and the writer knows of one instance in which an uncertainty of that order of magnitude in the orientation of his thin sections caused an author to waver between two opposed interpretations in a regional problem. If he had known the orientation within  $2^{\circ}$ , the interpretation would probably have been definite.

The apparatus illustrated and described below was devised by the writer for the purpose of orienting hand specimens accurately in the laboratory and measuring the orientations of joints, *s*-planes, and lineations, and marking planes of thin sections. The model described was the first one built and is necessarily a little awkward for some of the measurements. However, it does give a rapid measurement of the orientation of any plane or lineation in a rock more accurately than similar measurements can be made in the field. It is, therefore, deemed advisable to publish a description at this time with the hope that the apparatus will prove of immediate usefulness to the workers in fabric analysis, and that improvements in design that are sure to come will be made more quickly as a result of suggestions from these workers.

## DESCRIPTION OF APPARATUS

The apparatus consists of two separate pieces: 1. Table for holding a hand specimen. (Fig. 1, I.) 2. Measuring device. (Fig. 1, II.)

*Table.* The table for mounting hand specimens is very simple. It consists of a brass plate (Fig. 1, I, *A*), three inches square and one-fourth inch thick, mounted in the middle of a brass plate that is six inches square and one-half inch thick, *D*, by means of an ordinary ball and socket joint, *B*, like those used on tripods. The top of the upper plate is made

\* Given before the Mineralogical Society of America, December 29, 1936.



into a grid by cutting grooves one-fourth inch apart and one-sixteenth inch deep in it. This is a very effective method of holding the molding clay which, in turn, holds the specimen.

The *measuring device* consists essentially of three parts:

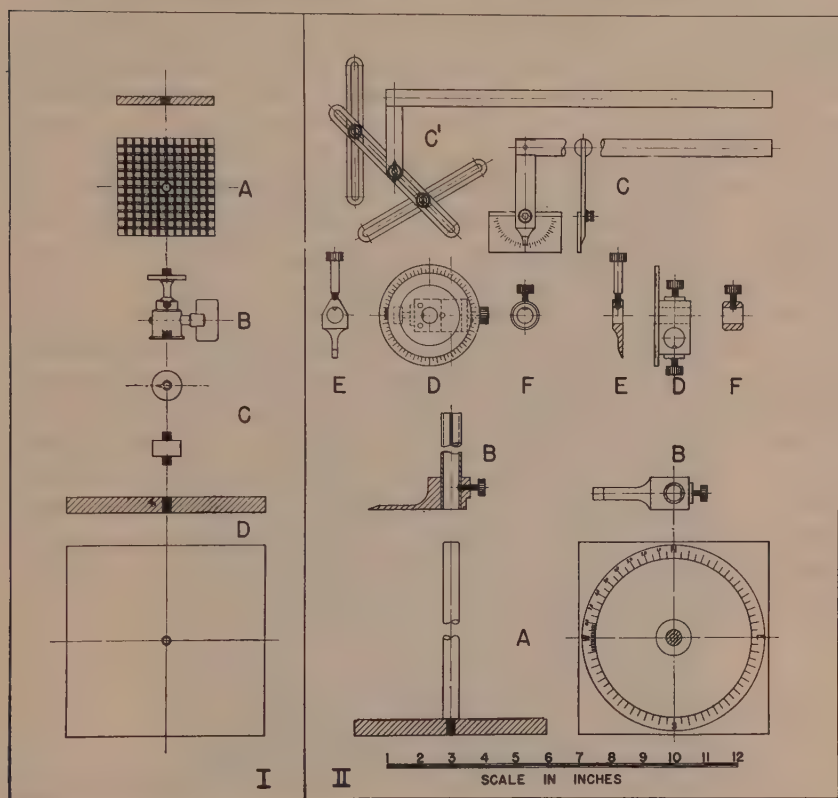


FIG. 1—Detail drawing of the orienting apparatus.

I—Mounting table.

II—Measuring device.

(a) A brass plate (Fig. 1, II, *A*), with a graduated circle from the center of which rises a one-half inch brass rod twelve inches long, normal to the plate. The four sides of the plate are marked *N*, *E*, *S*, and *W*, and the four quadrants are numbered independently.

(b) A brass tube, *B*, turns on the rod and there is a pointer brazed to it so that the two turn together. A set screw opposite the pointer can be tightened so that the tube and pointer are clamped in a given position. This pointer gives the strike readings. There is a groove in the outside

of the tube into which a screw of a right angle clamp, *D*, fits so that the clamp maintains a fixed relation to the tube and pointer. Through the other (a horizontal) hole of the clamp passes:

(c) A one-half inch brass rod, *C*, twelve inches long. To one end of the rod is fastened, by means of a three inch bar normal to the rod, a brass plate that is one and one-half by two inches and one-eighth inch thick. A set screw in the right angle clamp holds the rod (and plate) in any desired position. The rod is grooved and a pointer on a screw collar, *E*, rides the rod in such a position that it is always normal to the measuring plate. A vertical graduated circle is brazed to the clamp, *D*, with its zero point at the top so that the pointer, *E*, reads 0 when the measuring plate is horizontal. These readings obviously give the dips. A movable collar *F*, on the rod and opposite from the pointer keeps the rod from slipping through the clamp while it is being turned.

The end of the bar that holds the measuring plate serves as a pointer for the graduated semi-circle on the latter. When this pointer indicates zero the long edge of the plate is horizontal and is parallel to the rod that carries it, and hence to the pointer on *B*. Therefore, the readings on the circles of *D* and *A* give the dip and strike, respectively, for the plate. *C* may be replaced by a similar rod on which three slotted thin brass bars, *C'*, take the place of the plate. The bars may be moved in the plane of the plate and are oriented in the same manner. They are for marking the plane of a thin section on a hand specimen, or for determining the orientation of an *s*-plane.

#### PROCEDURE

The apparatus can be used for the following:

1. To orient a hand specimen for laboratory study.
2. To measure the orientation of a plane surface other than the one marked (e.g., a joint plane).
3. To measure the direction and angle of plunge of a lineation.
4. To mark a plane in a given position.
5. To measure the orientation of an *s*-plane or other plane that does not form a flat surface on the specimen.

1. The first step in marking or measuring a plane or lineation on a hand specimen is to orient the specimen. A specimen oriented in the field will necessarily have a more or less plane surface with arrows marked on it representing the dip and strike. To re-orient such a specimen in the laboratory it is only necessary to set the measuring plate at the proper dip and strike, mount the specimen on the table, and bring the marked surface parallel to the plate, with the strike arrow on the



specimen parallel to the long edge of the plate (Fig. 2). This is accomplished as follows:

(a) Turn the pointer on *B* so that it reads the strike and clamp it tightly.

(b) Turn the rod holding the measuring plate until the pointer on the vertical circle reads the proper dip. Clamp. In the example illustrated in Fig. 2 the face on the specimen strikes *N 69° E* and dips *27° SE*.

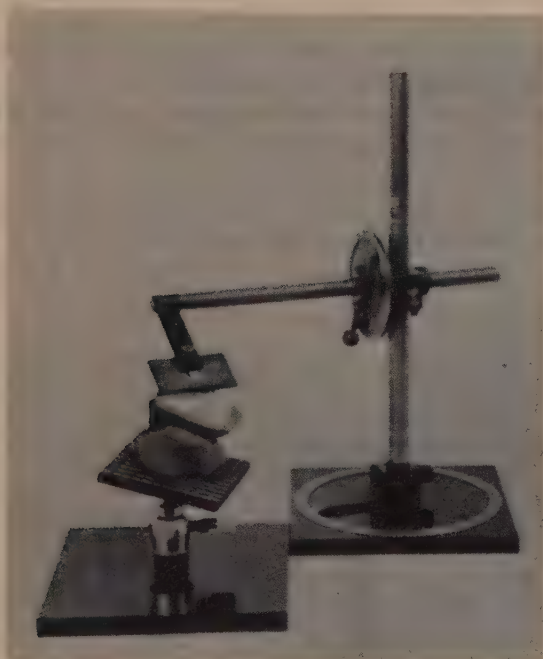


FIG. 2—Method of re-orienting a hand specimen in the laboratory.

(c) Mount the specimen on the table and place the table base against that of the measuring device in such a position that the specimen is brought as near to the plate as possible. Adjust the specimen in the clay so that the marked surface comes somewhere near parallel to the plate.

(d) Loosen the universal joint and adjust the table until the two surfaces are practically parallel. Re-clamp the universal joint.

(e) Adjust the height of the plate (without changing the orientation) so that it just touches the rock.

(f) Loosen the universal joint again and complete the orientation by turning the table slightly and moving the base of the table, if necessary. Be sure that the strike line on the specimen is parallel to the long edge of the plate.

2. To measure the orientation of another plane surface on a specimen after it has been oriented the following steps are taken:

(a) Move the mounting table to such a position that the face to be measured strikes approximately toward the upright rod of the measuring device.

(b) Release the tube and pointer (Fig. 1, II, *B*), and turn them until the measuring plate approaches the specimen.

(c) Release the rod, *C*, on which the measuring plate is fixed and turn it until the plate comes approximately parallel to the surface to be measured.

(d) Complete the measurement by moving the base of the mounting table slightly and/or adjusting the measuring plate.

(e) Read the dip and strike on the vertical and horizontal circles respectively.

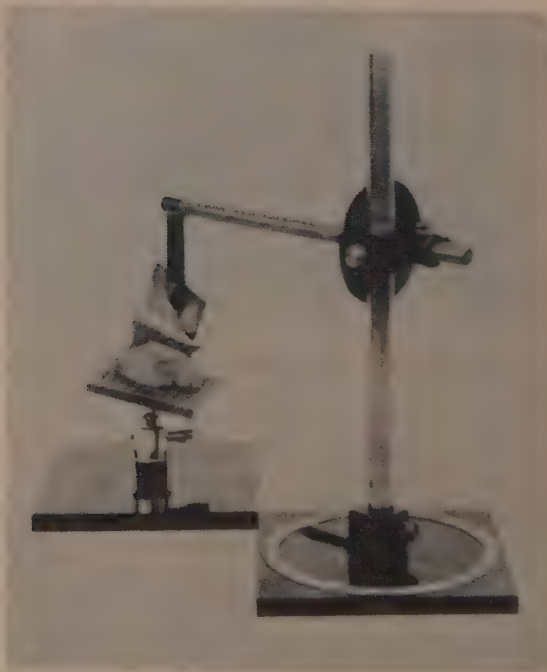


FIG. 3—Measurement of the direction and angle of plunge of a lineation ( $25^{\circ}$  S  $47^{\circ}$  E).



### 3. Measurement of a lineation.

(a) Direct measurement (Fig. 3); when the lineation lies in a plane surface:

(1) Fasten the dip plate so that it is vertical; i.e., so that the pointer, *E*, reads  $90^\circ$ .

(2) Move the mounting table so that the lineation plunges approximately toward the upright rod.

(3) Release the tube and its pointer and turn the measuring device until the measuring plate is directly over the lineation. It may be necessary to move the mounting table slightly.

(4) Loosen the plate itself so that it swings about its pivot and turn it until the lower edge of the plate is approximately parallel to the surface and hence to the lineation.

(5) Lower the plate until it just touches the specimen and make minor adjustments of the plate and/or mounting table until the edge of the plate and the lineation are as nearly parallel as possible.

(6) Read the direction of plunge on the graduated circle of the base, and the angle of plunge on the graduated semi-circle on the measuring plate. The lineation of the illustrative example, Fig. 3, plunges  $25^\circ S 47^\circ E$ .

If the lineation is not in a plane surface on the specimen the edge of the plate cannot be placed in contact with it. However, it can be placed more or less parallel to the lineation by manipulations similar to those described above. The degree of parallelism depends upon how well the lineation is developed and exposed. The plate touches the specimen at the lowest corner only.

(b) Graphic solution; convenient only when the lineation lies in the marked surface. If a specimen has just been oriented and the plate is still parallel to the surface it may be easier to make a graphic solution of the direction and angle of plunge of a lineation in that surface as follows:

(1) Free the measuring plate and turn it about the pivot until the long edge is parallel to the lineation. The angle indicated on the plate gives the deviation of the lineation from the strike. If the geographic coordinates are desired a graphic solution must be made. The simplest one, for fabric analysis, is made by using the Schmidt net:

(2) The projection of the plane surface is drawn on a piece of tracing paper placed over the Schmidt net. This is done by turning the paper until the point on the periphery that represents the north end of the strike line is at the north pole of the net and then drawing the great circle that is as many degrees from the periphery as the angle of dip.

(3) The projection of the lineation is then represented by a point on this great circle as many degree from the north, or south, pole of the net as the lineation deviates from the strike.

(4) To determine the direction of plunge of the lineation turn the tracing paper back to the zero position and draw the radius that passes through the point representing the projection of the lineation. The point where this radius strikes the periphery of the net gives the direction of plunge.

(5) To obtain the angle of plunge turn the tracing paper until the projection of the lineation is on the equator of the net. The number of degrees that it lies from the periphery of the net then gives the angle of plunge.

4. To mark the plane of a desired thin section (Fig. 4):

(a) Substitute the arm carrying the slotted bars,  $C'$ , for the one carrying the plate,  $C$ .

(b) Set the pointers for the desired dip and strike, as in 1.

(c) Move the mounting table, keeping constant orientation, until the specimen comes within the three bars. It may be necessary to adjust the height or length of  $C'$ .



FIG. 4—Measuring and marking the plane of a thin section. The apparatus has been turned  $180^\circ$  from its position in Figs. 2 and 3 in order to show the marking arms to better advantage. Plane of thin section,  $N 67^\circ W 89^\circ NE$ .



(d) Adjust the bars until they fit the specimen as closely as possible and mark the trace of the plane with a sharp pencil, using the bars as straight edges. Fig. 4 shows the apparatus set up for marking the plane of a thin section. See Fig. 5 for a graphic representation of the data for this specimen.

(e) Remove the specimen and complete the trace of the plane by drawing a line across the bottom of the specimen, using a flexible straight edge, and then mark the trace all the way around with a heavy line in India ink.

If it is desired to mark a thin section plane with respect to some structure in the rock, the simplest procedure is to make a graphic solution to obtain the geographic coordinates of the desired plane and then proceed as outlined above.

5. To measure the orientation of a plane that does not form a flat surface on the specimen:

(a) Move the mounting table until the plane to be measured strikes, as nearly as can be told, toward the upright rod of the measuring device.

(b) Release the tube and pointer, *B*, and turn the measuring device until the arms of *C'* can be placed around the specimen. Release the rod carrying the arms and turn them until their plane approximately coincides with the one that is being measured.

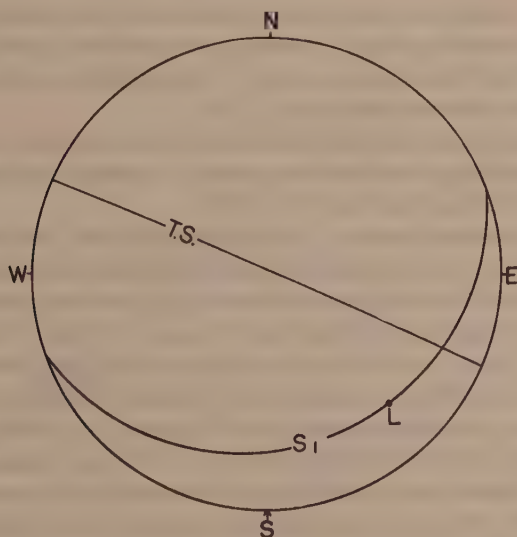


FIG. 5—Graphic representation on an equal area projection of the data measured for the illustrative specimen in Figs. 2, 3, and 4.

(c) Shift the table base and/or rod carrying the arms until they can be fitted to the plane to be measured on two or three sides of the specimen.

(d) Read the dip and strike of the plane on the vertical and horizontal circles, respectively.

Figures 2-4 show the apparatus set up for various measurements, as indicated in the legends and Fig. 5 shows the data plotted on a Schmidt net.

*Improved measuring device.*—The second model constructed is a decided improvement over the original one. Its description is included as a supplement to, rather than replacing, that of the original, because the latter is so much easier to make. Many shops are not equipped to construct the improved model, but its ease of operation more than justifies the extra effort required to build it, if it is at all possible.

Figure 6, I shows the improved model set up to orient a specimen; Fig. 6, II is a detail drawing of the parts that are essentially different from those of the first model. There are three important changes:

(1) Keys and keyways replace the slots and pointed screws that hold the pointer, *E*, of the original model and the right angle clamp and attached vertical circle, *D*, in constant relation to the rod, *C*, and the tube of *B*, respectively (see Fig. 1, II, and Fig. 6, II). This arrangement makes it impossible to get a wrong reading with either of the pointers.

(2) A keyed collar has been put in the side of the right angle clamp carrying the measuring arm, *C*, making it possible to vary the length of the arm without loosening a screw, or changing the orientation of the measuring plate or arms (see Fig. 6, II, *J*).

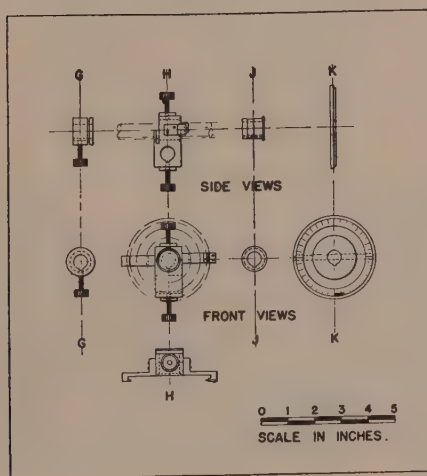
(3) The measuring arms and plate have been attached to the same rod so that no change of parts is necessary to orient a specimen or mark the plane of a thin section (see Fig. 6, I).

*Marking of oriented sections.*—It is important that the orientation of a thin section not only be measured and recorded accurately, but that it be marked on the thin section itself so that it can be oriented properly during the subsequent study and can be used by other workers, if occasion arises. If one knows the dip and strike of the plane of a thin section and knows which direction he is looking through it, then a single arrow fixes its orientation completely. However, it is very easy for a thin section to become inverted while it is being prepared, or even during mounting on a universal stage, so it is safer to have two directions marked on each section to obviate the possibility of inversion. The thin sections should be mounted so that one looks through them at the surfaces of the rock from which they are cut.





I



II

FIG. 6—I, improved model; II, detail drawing of the parts that are different from those of the original model.

If the positions of the fabric axes are known before the thin sections are cut it is customary to have the arrows parallel to the fabric axes. Sections cut normal to the *a*- or to the *b*-axis should have their arrows parallel to the *c*-axis, and to the length of the thin section, with the barbs toward the upper (positive) end of the *c*-axis. The other direction marked on the section normal to the *a*-axis is indicated by a short line without barbs, normal to the arrow, and on the side of  $+b$ . That on the section normal to *b* is toward  $+a$ . The arrow on the section normal to the *c*-axis should be parallel to the *a*-axis, with the barbs toward the front (positive) end, and with the auxiliary line on the side of  $+b$ . These orientations are based on the conception that the fabric axes are placed for study as the corresponding axes of a crystal would be. Such an orientation is convenient, but by no means essential. It is shorter to refer to thin sections by the names of the axes to which they are normal. Thus, the "*a* section," the "*bc* section," and "the section normal to the *a*-axis" are synonymous.

The sketches of Fig. 7 will make clear the suggested system for marking thin sections. The letters enclosed by parentheses are not marked on the actual thin sections; they are put on the sketches to indicate the directions of the arrows and lines for the different sections. If the positions of the axes are not known the dip and strike marked on a section fix its orientation. The actual marking may be with reference to fabric axes, prominent structures, or geographic coordinates. It makes no difference as long as the worker has enough data recorded so that he can relate all of these things to each other in the integration of his results.

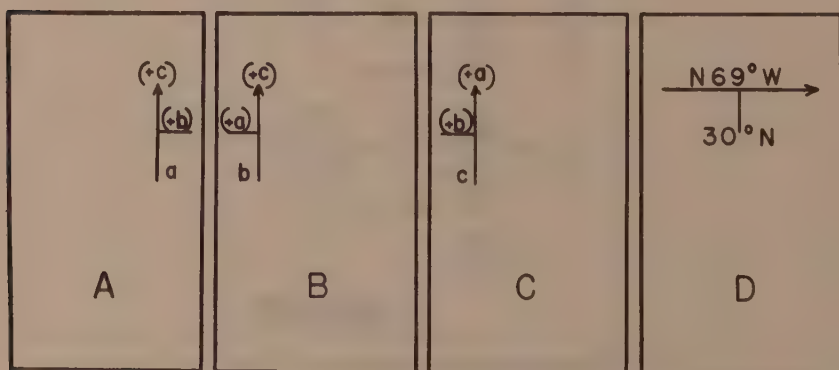


FIG. 7—Suggested method of marking thin sections. A, B, C, with respect to fabric axes. D, with respect to geographic coordinates. The letters in parentheses are not marked on the actual thin sections.



If one has a saw available so that the plane of the thin section may be smoothed off, the directions may be drawn directly on the surface for the thin section marker. If, however, the directions must be indicated on the rough specimen, the measuring device may be used to good advantage. A line may be drawn on the specimen in such a position that its points of intersection with the plane of the thin section determine the direction of the arrow on the thin section. Such a line should be drawn only on the part of the specimen through which it is desired to look at the finished thin section. Its orientation is fixed by measuring and recording the orientation of the plane that it determines. A different color of ink or pencil or different kind of line will distinguish this line from that of the thin section itself. The direction that the arrow is to point may be indicated by barbs on the line, and the auxiliary orienting line drawn on the proper side. It may be made a little more certain by marking the side of the specimen toward which the arrow is to point,  $\odot$ , and the opposite side,  $\oplus$ . Figure 8 shows a specimen marked in this manner.

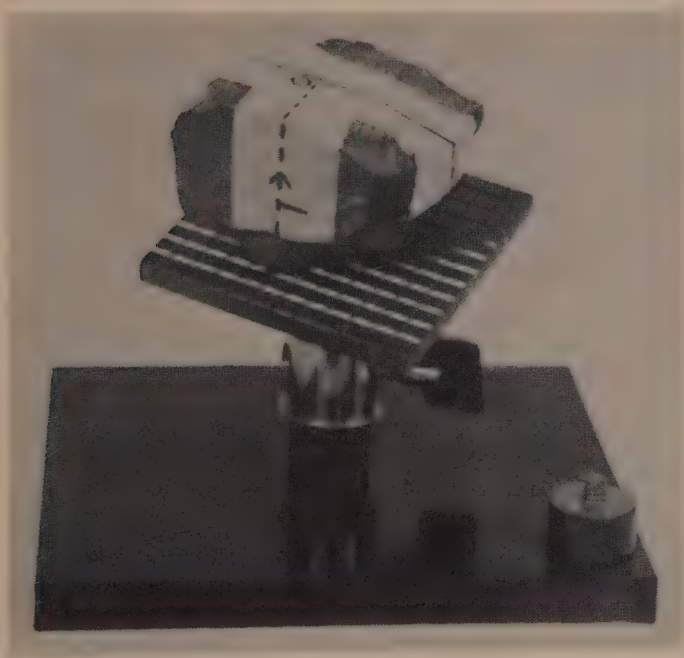


FIG. 8—Hand specimen marked in the suggested manner. The solid line is the plane of the thin section and the dashed line gives the direction of the arrow.

The actual sawing of a specimen along a given line is facilitated by having a machinist's flexible vise with spring-controlled "fingers" mounted in connection with a diamond, or carborundum, saw. Such a vise will hold an irregularly shaped specimen in any position. It is mounted so that it can be moved along two horizontal tracks that are at right angles to each other. The specimen is gripped in the vise with the plane of the desired thin section parallel to the plane of the saw and the vise is moved until the saw will cut the specimen at the desired place.



# THE CRYSTAL STRUCTURE OF ALUNITE AND THE JAROSITES

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Alunite is of potential economic value in the United States as a source of both aluminum and potassium compounds. Various attempts have been made to exploit the extensive deposits at Marysville, Utah, and the U. S. Bureau of Mines is now studying the subject. A determination of the crystal structure of alunite was undertaken at the suggestion of Mr. J. Koster of that Bureau.

Alunite and the related jarosites are of mineralogical interest on account of the many types of isomorphous replacements shown by them. The composition of the various members has been summarized by Schaller<sup>1</sup> as follows:

## *Sulphates*

Alunite	(Al(OH) <sub>2</sub> ) <sub>6</sub>	K <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>
Natroalunite	(Al(OH) <sub>2</sub> ) <sub>6</sub>	Na <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>
Jarosite	(Fe(OH) <sub>2</sub> ) <sub>6</sub>	K <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>
Natrojarosite	(Fe(OH) <sub>2</sub> ) <sub>6</sub>	Na <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>
Plumbojarosite	(Fe(OH) <sub>2</sub> ) <sub>6</sub>	Pb	(SO <sub>4</sub> ) <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>
Karphosiderite	(Fe(OH) <sub>2</sub> ) <sub>6</sub>	H <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>

## *Phosphates*

Hamlinite	(Al(OH) <sub>2</sub> ) <sub>6</sub>	Sr	(HPO <sub>4</sub> ) <sub>2</sub>	(Sr(PO <sub>4</sub> ) <sub>2</sub> )
Plumbogummite	(Al(OH) <sub>2</sub> ) <sub>6</sub>	Pb	(HPO <sub>4</sub> ) <sub>2</sub>	(Pb(PO <sub>4</sub> ) <sub>2</sub> )
Gorceixite	(Al(OH) <sub>2</sub> ) <sub>4</sub>	Ba	(HPO <sub>4</sub> ) <sub>2</sub>	(Ba(PO <sub>4</sub> ) <sub>2</sub> )
Florencite	(Al(OH) <sub>2</sub> ) <sub>6</sub>	Ce <sub>2/3</sub>	(Ce <sub>1/3</sub> PO <sub>4</sub> ) <sub>2</sub>	(Ce <sub>2/3</sub> (PO <sub>4</sub> ) <sub>2</sub> )

## *Sulphate-Phosphates*

Beudantite	(Fe(OH) <sub>2</sub> ) <sub>6</sub>	Pb	(SO <sub>4</sub> ) <sub>2</sub>	Pb(AsO <sub>4</sub> ) <sub>2</sub>
Corkite	(Fe(OH) <sub>2</sub> ) <sub>6</sub>	Pb	(SO <sub>4</sub> ) <sub>2</sub>	(Pb(PO <sub>4</sub> ) <sub>2</sub> )
Svanbergite	(Al(OH) <sub>2</sub> ) <sub>6</sub>	Sr	(SO <sub>4</sub> ) <sub>2</sub>	(Sr(PO <sub>4</sub> ) <sub>2</sub> )
Hinsdalite	(Al(OH) <sub>2</sub> ) <sub>6</sub>	Pb	(SO <sub>4</sub> ) <sub>2</sub>	(Pb(PO <sub>4</sub> ) <sub>2</sub> )
Harttite	{ (Al(OH) <sub>2</sub> ) <sub>6</sub>	Sr	(SO <sub>4</sub> ) <sub>2</sub>	(SO <sub>4</sub> ) <sub>2</sub>
	{ 2(Al(OH) <sub>2</sub> ) <sub>6</sub>	Sr	(HPO <sub>4</sub> ) <sub>2</sub>	(Sr(PO <sub>4</sub> ) <sub>2</sub> )

Artificial jarosites containing rubidium have also been prepared.<sup>2</sup> In addition to these substances the compound  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ , a solid phase in the system  $\text{Fe}_2\text{O}_3\text{--SO}_2\text{--H}_2\text{O}$ , is also probably a jarosite and possibly corresponds to the mineral borgströmite.<sup>3</sup> The results of the crystal analysis lead to a structural explanation for these various replacements.

<sup>1</sup> Schaller, *U. S. Geol. Survey, Bull.* **509**, p. 76, 1912. *Zeits. Kryst.*, vol. **50**, p. 106, 1912. *Am. Jour. Sci.*, vol. **32**, p. 359, 1911.

<sup>2</sup> Fairchild, *Am. Mineral.* vol. **18**, p. 543, 1933.

<sup>3</sup> Posnjak and Merwin, *Jour. Am. Chem. Soc.*, vol. **44**, p. 1977, 1922.

From the structural and chemical point of view these minerals are of interest in that they are basic salts in which hydroxyl binding<sup>4</sup> might be expected. Their behavior upon heating<sup>5</sup> should be explained by their structures.

#### SOURCE OF MATERIALS

The work was greatly facilitated by the excellent material available for study. Dr. W. F. Foshag of the U. S. National Museum kindly furnished crystals of alunite (USNMR 6290) from Rosita Hills, Colorado, and jarosite (USNMR 6299) from Meadow Valley Mine, Pioche, Nevada. These crystals, which were from the Roebling collection, showed predominant development of  $c(00.1)$  and  $r(10.1)$ . They measured as much as 2 mm. on the edge and a number of well formed ones about  $.3 \times .3 \times .1$  mm. were selected for  $x$ -ray work. Dr. Foshag also supplied samples of the original analyzed natrojarosite<sup>6</sup> (USNM 86932), analyzed ammoniojarosite<sup>7</sup> (USNM 95654) from Panguitch, Utah, plumbojarosite from the original locality, Cook's Peak, New Mexico<sup>6</sup> (USNMR 6308), karpfoserite (USNMR 6266) from Greenland, borgströmite (USNMR 6312) from Otravaara, Finland, and hamlinite (USNMR 4051) from Serra de Congonhas Minas Geraes, Brazil. The samples of ammoniojarosite, karpfoserite, and borgströmite were microcrystalline. Individual crystals of natro- and plumbojarosite measured about  $.08 \times .08 \times .01$  mm. and those of the other minerals were as large as 1 mm. Crystals of plumbojarosite, from the Tintic Standard Mine, Dividend Utah, measuring as much as 0.5 mm. on the edge were supplied by Dr. W. T. Schaller of the U. S. Geological Survey.

Mr. J. G. Fairchild of the U. S. Geological Survey very kindly supplied samples of microcrystalline artificial silver and lead jarosites.<sup>2</sup> Dr. E. Posnjak of the Geophysical Laboratory, Carnegie Institution of Washington, furnished single crystals of the compound  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$  that he had prepared. Analyzed samples of commercial grades of alunite from Marysville, Utah, containing from 1.2 to 45.0%  $\text{SiO}_2$  were made available by Mr. J. Koster of the U. S. Bureau of Mines.

#### EXPERIMENTAL PROCEDURE, LATTICE DIMENSIONS AND SPACE GROUP

Lattice dimensions of alunite were obtained from layer line photographs about the orthohexagonal  $c$  and  $a$  axes and from high angle

<sup>4</sup> For a discussion of the role of hydroxyl binding in structural chemistry see Bernal and Megaw, *Proc. Roy. Soc.*, vol. **A151**, p. 384, 1935.

<sup>5</sup> Fink, Van Horn, and Pazour, *Ind. Eng. Chem.* vol. **23**, p. 1248, 1931.

<sup>6</sup> Hillebrand and Penfield, *Am. Jour. Sci.* (5), vol. **14**, p. 211, 1902.

<sup>7</sup> Shannon, *Proc. U. S. National Museum* #2758, 1928.

reflections from (*h**k*.0) and (00.1) on Weissenberg photographs. These dimensions are listed in Table 1 together with the results obtained from the other minerals that were examined. The value of *c/a* for alunite agrees to within the limit of experimental error with  $2 \times c/a$  as obtained from reflection goniometer measurements. Weissenberg photographs were taken with at least two different crystal orientations for jarosite, natrojarosite and  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ , and powder photographs were made, with FeK radiation, from these minerals as well as from argento- and ammoniojarosites, karpfoserite, borgströmite, and hamlinite. Agreement between *x*-ray and reflection goniometer measurements for jarosite is very poor and considerably exceeds the apparent experimental error.

TABLE 1

Mineral	Composition	Lattice dimensions		<i>c/a</i>			Density	
		<i>a</i>	<i>c</i>	<i>x</i> -ray	Morpho- logical	<i>x</i> -ray <i>n</i>	calc.	obs.
Alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_3$	6.96	17.35	2.492	1.252	1.246	2.80	2.75
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	7.20	17.00	2.361	1.245	1.18	3.24	3.26
Argento- jarosite <sup>1</sup>	$\text{AgFe}_3(\text{SO}_4)_2(\text{OH})_6$	7.22	16.40	2.27	1.106 <sup>5</sup>	1.13	3.80	
Natro- jarosite <sup>2</sup>	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$	7.18	16.30	2.27	1.104	1.13	3.29	3.2
Ammonio- jarosite <sup>3</sup>	$\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$	7.20	17.00	2.36			3.09	
Plumbo- jarosite <sup>4</sup>	$\text{Pb}(\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6)_2$	7.20	33.60	4.67	1.147 <sup>5</sup>	1.17	3.71	3.67
— <sup>1</sup>	$\text{H}_2\text{OF}_3(\text{SO}_4)_2(\text{OH})_3\text{H}_2\text{O}$	7.16	16.90	2.36	1.14	1.18		

<sup>1</sup> Synthetic materials.

<sup>2</sup> Analysis 6.28%  $\text{Na}_2\text{O}$ , 0.37%  $\text{K}_2\text{O}$  (Hillebrand).

<sup>3</sup> Analysis 0.22%  $\text{Na}_2\text{O}$ , 1.56%  $\text{K}_2\text{O}$ , 4.23%  $(\text{NH}_4)_2\text{O}$  (Shannon).

<sup>4</sup> Crystals from the two localities mentioned in the introduction gave closely the same constants.

<sup>5</sup> Unpublished data from Dr. W. T. Schaller.

Failure of obtaining agreement in crystallographic constants as measured on optical and *x*-ray goniometers is probably due to difficulties in both methods. In substances, such as the jarosites, in which extensive solid solution formation is possible, individual crystals might show zoning in composition, particularly on the surface and thus give fortuitous, but consistent, values for crystal angles. While *x*-ray measurements are not susceptible to this error they are influenced by the fact



that observations are made on only a few crystals. Even though the sample is an analyzed one the individual crystals selected for study might show considerable departure in composition from the mass of the material, particularly since preference is given to very well formed ones. Measurement of refractive indices for the crystal examined can partially protect against such error.<sup>8</sup>

Dr. W. T. Schaller of the U. S. Geological Survey has graciously given permission to quote from unpublished work by him as follows. "Axial ratios obtained on crystals of argento- and plumbojarosites from the Tintic Standard Mine, Dividend, Utah, are  $c/a = 1.106$  and  $1.147$ , respectively. Individual crystals gave fair signals but the reflections were not entirely satisfactory." The value found for plumbojarosite is considerably lower than that given by Penfield,<sup>6</sup> namely  $1.216$ ; it agrees with the  $x$ -ray goniometer measurements within the limits of error of the two measurements.

Observed and calculated densities are in close agreement for all the compounds save natrojarosite. Experimental determination of density is of course always open to serious error and the best procedure is to take the maximum value obtained provided the material is homogeneous. This has been done for the observed values of Table 1 which are all taken from the literature.

Laue photographs of alunite made with the  $x$ -ray beam accurately normal to (00.1) showed the symmetry  $D_{3d}-3m$ . Various sized crystals of alunite, jarosite, plumbojarosite, hamlinite, and  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$  did not give a piezoelectric effect when tested by the method of Giebe and Scheibe.<sup>9</sup> Individual crystals of alunite and jarosite showed strong pyroelectric properties when tested after the Martin method.<sup>10</sup> It should be emphasized here that a negative pyroelectric or piezoelectric test is without significance for determination of crystal symmetry.

All the minerals examined gave reflections from  $(h\bar{h}l)$  with  $l$  odd and absences from all planes having  $(h-k+l) = 3n$ . The space group based on this criterion and the crystal symmetry as shown by Laue and Weissenberg photographs is  $D_3^7-R32$ ,  $C_{3v}^5-R3m$ , or  $D_{3d}^5-R\bar{3}m$ . Intensities of  $(hk.0)$  for the jarosites could not be explained by  $R32$ . The observation that alunite is pyroelectric requires its space group to be  $C_{3v}^5-R3m$  and the univalent jarosites probably have the same structure.

<sup>8</sup> This discussion is based upon conversations with Dr. H. E. Merwin of the Geophysical Laboratory, Carnegie Institution of Washington.

<sup>9</sup> Giebe and Scheibe, *Zeits. phys.*, vol. **33**, p. 760, 1925.

<sup>10</sup> Martin, A. J. P., *Mineral. Mag.*, vol. **22**, p. 519, 1931.

## STRUCTURE DETERMINATION FOR ALUNITE AND JAROSITE

The rhombohedral unit of structure contains  $1R'R''_3(SO_4)_2(OH)_6$ . In the space group  $R\bar{3}m^{11}$  referred to hexagonal axes there are sets of three equivalent positions on the three fold axes at  $00z$ , nine equivalent ones about these axes at  $x\bar{x}z$ ,  $x2xx$ ,  $2\bar{x}\bar{x}z$  and the eighteen general positions. Potassium atoms can be placed at  $000$  and two sets of  $S$  and  $O$  atoms of  $SO_4$  groups are on the trigonal axes,  $00z$ . Aluminum, or iron, atoms and two sets of oxygen atoms of  $SO_4$  groups are in the nine equivalent positions.

The  $SO_4$  groups are assumed to have the dimensions found in other sulfates,<sup>12</sup> the S-O distance being 1.52Å. There are two possible orientations in both the  $a$  and  $c$  directions for each set of sulfate groups. The only parameters in the  $a$  direction are those of the hydroxyl groups and the  $R''$  atoms. Consideration of the  $(hk.0)$  reflections from jarosite shows that  $x_{Fe} = .167$ . With this limitation the intensities of  $(hk.0)$  for alunite require the two sets of  $SO_4$  groups to be rotated  $60^\circ$  with respect to one another in the projection on  $(00.1)$  and the hydroxyl groups to be in two non-equivalent sets with  $x_{OH}$  near .13 and  $-.13$ . Parameter values in the  $c$  direction can be fixed from this projection, an approximate knowledge of interatomic distances, and the intensities of the  $(00.1)$  reflections. Final parameter values for alunite are:

	$x$	$z$		$x$	$z$		$x$	$z$
3 K		0	3 $O_1'$		.060	9 OH	-.150	.126
3 $S'$		.305	3 $O_1''$		-.060	9 OH	.150	-.126
3 $S''$		-.305	9 $O'$	-.215	-.058			
3 Al	.167	.167	9 $O''$	.215	.058			

These values are to be slightly changed for jarosite, but because of the predominant effect of iron correct ones cannot be found from the  $x$ -ray data. Calculated values of  $F^2/100$  for some reflections from alunite and jarosite are listed together with observed intensities in Table 2. Scattering factors used from  $\sin \theta/\lambda = .10$  to  $.30$  for  $Al^{+++}$  and  $O^{--}$  are those given by Wyckoff,<sup>13</sup> other values were taken from the *I.T.D.C.S.* No temperature correction was made in the calculations.

<sup>11</sup> *The International Tables for the Determination of Crystal Structures*, Chemical Catalogue Company, New York, 1935, are used throughout. (Later referred to as *I.T.D.C.S.*)

<sup>12</sup> *Strukturbericht II, Ergänzungsband II*, Leipzig 1936. See also C. A. Beevers and C. M. Schwartz, *Zeits. Krist.*, vol. 91, p. 157, 1935. W. A. Wooster, *ibid.*, vol. 94, p. 375, 1936.

<sup>13</sup> Wyckoff, R. W. G., *The Structure of Crystals*, p. 100. New York, 1931.

TABLE 2. CALCULATED VALUES OF  $F^2/100$  AND ESTIMATED INTENSITIES OF REFLECTION

Jarosite			Alunite		
Plane	$F^2/100$	Estimated Int. MoK	Plane	$F^2/100$	Estimated Int. NiK
12.0	50	mw		100	s
24.0	700	vs		400	vs
36.0	210	m		250	s
48.0	250	m		120	s
5 10.0	40	vw	3 3.0	1	a
6 12.0	220	mw	6 6.0	100	s
7 14.0	10	a	5 4.0	50	mw
8 16.0	100	w	7 8.0	50	w
MoK FeK			CuK		
00.3	131	ms		6	w
00.6	200	s		37	ms
00.9	210	ms		66	ms
00.12	36	a		3	a
00.15	23	a		3	a
00.18	82	w		21	mw
1 1.1	330			230	s
2 2.2	100	ms		2	vw
3 3.3	21	w		5	w
4 4.4	90	ms		110	ms
5 5.5	1	a		5	w
6 6.6	145	m	2 2.1	145	s
7 7.7	40	w	2 2.4	105	m
8 8.8	65	w	2 2.7	57	w
9 9.9	6	a	1 1.2	48	ms
10 10.10	82	mw	1 1.4	9	a
11 11.11	4	a	1 1.5	26	mw
12 12.12	26	w	3 3.3	380	vs

## STRUCTURE DETERMINATION FOR PLUMBOJAROSITE

Equatorial zone Weissenberg photographs were taken about the  $c$  axis and the normal to (12.0), FeK radiation being used. Data from the latter are listed in Table 3. The lattice is rhombohedral and the unit of structure contains one  $\text{Pb}[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]_2$ . The value of  $a_0$  (hexagonal cell) for plumbojarosite is closely the same as that of jarosite while  $c_0$  is approximately twice as great.



TABLE 3. WEISSENBERG PHOTOGRAPHIC DATA FROM PLUMBOJAROSITE, FeK RADIATION

$n$	$(00.(3n+3))$	$(10.(3n+2))$	$(20.(3n+1))$	$(30.3n)$	$(40.(3n+2))$	$(50.(3n+1))$	$(50.3n)$
0	m	s	m	vw	vw	a	m-ms
1	vw	ms	ms-s	vw-w	a	a	a
2	m	a	w	mw	m	a	a
3	vs	vw	vw	w-vw	a	a	a
4	w	ms-s	w	vw	a	a	m
5	mw	vw	mw	a	a	a	
6	mw	w	a	a	m		
7	w	a	vw	a	a		
8	a	mw	vw	mw-w	a		
9	a	vw	mw	vw			
10	w-mw	w	a	mw-w			
	$(10.(3n-1))$	$(20.(3n-2))$	$(30.3n)$				
0	s	s	vw				
1	mw	m	mw				
2	m	s	s				
3	a	w	w				
4	vw	vw	vw				
5	a	a	vw				
6	w	ms	m				
7	w	a	a				
8	vw	a	a				
9	a	w					
10	w	ms					

Since the ionic radius of  $Pb^{++}$  differs but slightly from that of  $K^{+}$  it would be expected that the plumbojarosite structure would differ from that of jarosite by replacement of half the potassium atoms with lead atoms, the other half of the positions remaining vacant and the remainder of the structure practically undisturbed. Such a change, however, increases the symmetry to that of the point group  $D_{3d}-\bar{3}m$ , the space group being  $D_{3d}^5-R\bar{3}m$ . Lead atoms without loss of generality are at  $000$ ;  $\frac{1}{3}\frac{2}{3}\frac{1}{3}$ ;  $\frac{2}{3}\frac{1}{3}\frac{2}{3}$ ; and iron atoms are at  $18(h)$  (*I.T.D.C.S.*) with  $x=.167$  and  $z=.417$ . This is strikingly shown by the fact that strong reflections are present from planes having complex indices only when  $(h/6+5l/12)=n$ ; thus:

(10.2)s	(20.4)ms-s	(30.6)mw	(40.8)m
(10.14)ms-s	(20.16)mw		(40.8)m
(10.26)mw	(20.28)mw	(30.30)mw-w	

If the remainder of the plumbojarosite structure was unchanged from that of jarosite reflections from  $(h0.l)$  with  $l$  odd should show, for particular values of  $h$ , normal decline of  $F$  as  $l$  increases, since lead atoms alone would contribute to such reflections. This is not quite true as perhaps

can be seen from the intensities of (00.*l*), thus 3rd m, 9th m, 15th w, 21st mw, 27th a. These rather suggest that the SO<sub>4</sub> and possibly the OH groups about the vacant potassium positions are slightly displaced along the *c* axis, by an amount, however, that probably does not exceed .01 *c*<sub>0</sub> = .34Å.

STRUCTURES OF NATRO-, ARGENTO-, AMMONIOJAROSITES,  
HAMLINITE, KAPHOSIDERITE, BORGSTRÖMITE,  
AND 3Fe<sub>2</sub>O<sub>3</sub>·4SO<sub>3</sub>·9H<sub>2</sub>O.

Powder photographs with FeK radiation of these minerals showed that they all are correctly classified as jarosites. The photograph of 3Fe<sub>2</sub>O<sub>3</sub>·4SO<sub>3</sub>·9H<sub>2</sub>O in particular was very closely similar to that of jarosite. Borgströmite gave a powder photograph closely related to these but distinctly different from them. Limited isomorphous replacement in the natural mineral is sufficient to account for the observed differences. This is also true for kaphosiderite the diffraction pattern of which is distinctly different from that of any of the above mentioned minerals. Powder photographs of hamlinite, on the other hand, showed considerable displacement of the interference maxima and change of intensities from those of the jarosites. These changes are to be expected as a result of replacing Fe<sup>+++</sup> by Al<sup>+++</sup>. In the absence of analyses it was thought unwise to use these powder diffraction data for determination of lattice dimensions. The argento- and ammoniojarosites, however, were materials of known composition. Lattice dimensions obtained from their powder diffraction data are listed in Table 1.

Equatorial zone Weissenberg photographs (FeK radiation) about the normal to (10.0) and to (0 $\bar{1}$ .0) showed that the structure of 3Fe<sub>2</sub>O<sub>3</sub>·4SO<sub>3</sub>·9H<sub>2</sub>O must be closely the same as that of jarosite. The rhombohedral unit of structure thus contains one Fe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>·4½H<sub>2</sub>O which corresponds to Fe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>5</sub>·2H<sub>2</sub>O. This change in composition is brought about without apparent change of symmetry or change in the parameter values for jarosite. It would seem, therefore, that half of the H<sub>2</sub>O molecules replace potassium at 000 $\bar{5}$  and that of the other half replace hydroxyl groups in a random manner.

## DISCUSSION

The structure of alunite projected to scale on (00.1) is shown as Fig. 1. In Fig. 2 an attempt has been made to show the immediate surroundings of some atoms. Inspection of these figures and consideration of the structure as a whole show that electrostatic requirements are well satisfied. An Al<sup>+</sup><sub>3</sub> ion is at the maximum possible distance, permitted by the

crystal symmetry, from other  $\text{Al}^{+3}$  ions and near the maximum possible distance from  $\text{S}^{+6}$  that still permits an  $\text{Al}^{+3}$  to oxygen of  $\text{SO}_4^{--}$  distance of *ca.*  $2.0\text{\AA}$ . Aluminum has the expected coordination number, six, being surrounded at the corners of an approximately regular octahedron by four  $\text{OH}^-$  groups and two oxygen atoms of  $\text{SO}_4^{--}$  ions. The coordination number of potassium is twelve, there being six oxygen atoms at  $2.80\text{\AA}$  and six hydroxyl groups at  $2.85\text{\AA}$ .

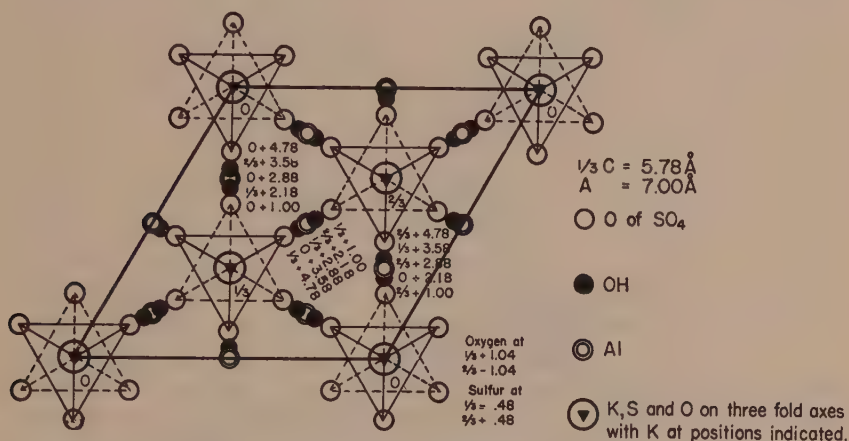


FIG. 1—Projection of the alunite structure in (00.1). Distances above the plane of projection are indicated on the figure.

Sulfate oxygen atoms on trigonal axes are surrounded by three  $\text{OH}^-$  groups at  $2.52\text{\AA}$ , the error being possibly as great as  $0.15\text{\AA}$ . It would seem that the hydrogen atoms must be so placed as to give hydroxyl binding to these oxygen atoms since no other ions, other than  $\text{S}^{+6}$ , approach them closely. Hydroxyl groups are near: 2 Al at  $2.04\text{\AA}$ , 1 K at  $2.85\text{\AA}$ , 1 oxygen at  $2.52\text{\AA}$ , 2 oxygen at  $2.65\text{\AA}$ , two other hydroxyl groups at  $2.65\text{\AA}$ , and two other hydroxyl groups at  $2.68\text{\AA}$ . These distances are near the expected values.

Before discussing the isomorphous replacements leading to the various minerals it might be best to list the ionic radii of the elements involved: these, as taken from Pauling<sup>14</sup> are:

$\text{Na}^+$	0.95Å	$\text{Pb}^{++}$	1.21	$\text{Ce}^{+++}$	1.18	$\text{S}^{+6}$	0.29
$\text{K}^+$	1.33	$\text{Sr}^{++}$	1.13	$\text{Al}^{+++}$	0.50	$\text{P}^{+5}$	0.34
$\text{Rb}^+$	1.48	$\text{Ba}^{++}$	1.35	$\text{Fe}^{+++}$	0.67	$\text{As}^{+5}$	0.47
$\text{Ag}^+$	1.26						

<sup>14</sup> Pauling, *Jour. Am. Chem. Soc.*, vol. 49, p. 765, 1927.



It is to be noted that the  $\text{SO}_4^{--}$ ,  $\text{PO}_4^{--}$ , and  $\text{AsO}_4^{--}$  differ but slightly in dimensions and that the positive ions  $\text{Na}^+$  to  $\text{Ce}^{+++}$  vary from  $r = 0.95\text{\AA}$  to  $1.48\text{\AA}$ , which is considerably greater than usually is found in an isomorphous series.

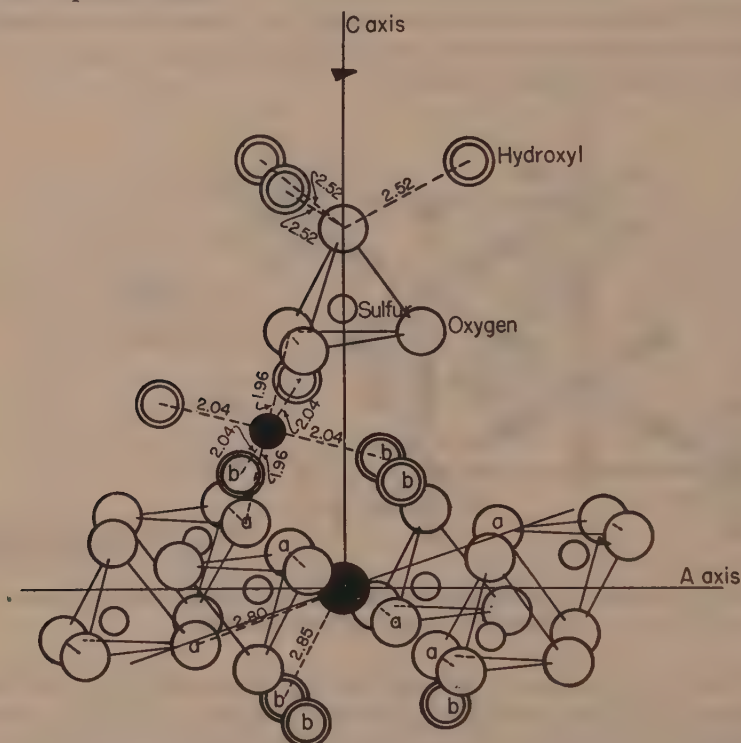


FIG. 2—The surroundings of potassium (large black circles), aluminum (small black circles), and oxygen at 00z. Potassium is at the indicated distances from six oxygen atoms of  $\text{SO}_4$  groups (marked *a*) and six hydroxyl groups (marked *b*).

The various  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Ag}^+$ ,  $\text{NH}_4^+$ ,  $\text{Fe}^{+++}$ , and  $\text{Al}^{+++}$  minerals, alunite, jarosite, natroalunite, argentojarosite, ammoniojarosite, and natrojarosite, are of course simple replacement compounds. Large variation in the ionic radii of the ion in the potassium position is allowed by the structure. In the case of plumbojarosite, as mentioned above, one  $\text{Pb}^{++}$  replaces  $\text{K}^+$  and the other  $\text{K}^+$  position remains vacant. It is possible that this vacant position is sometimes filled with a water molecule. In the sulfate-phosphates, beudantite, corkite, svanbergite, hinsdalite, and harttite replacement of  $\text{SO}_4^{--}$  by  $\text{PO}_4^{--}$  or  $\text{AsO}_4^{--}$  is accompanied by the filling of this vacant position with  $\text{Sr}^{++}$  or  $\text{Pb}^{++}$ , the limit being the 1:1 ratio of  $\text{SO}_4$  to  $\text{PO}_4$  or  $\text{AsO}_4$ . The cerium compound, the mineral florencite, is a continuation of this series in which  $\text{PO}_4^{--}$  replaces

$\text{SO}_4^{--}$  and  $\text{Ce}^{+++}$  the  $\text{K}^+$  ions;  $4\text{PO}_4^{---} + 2\text{Ce}^{+++}$  having the same charge as  $4\text{SO}_4^{--} + 2\text{K}^+$  and occupying the same positions.

The most interesting isomorphous replacement of all is that afforded by  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ . This compound can be written as  $\text{H}_2\text{O} \cdot \text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$  to show its relationship to jarosite  $\text{K Fe}_3(\text{SO}_4)_2(\text{OH})_5(\text{OH})$ . Thus an  $\text{H}_2\text{O}$  molecule replaces  $\text{K}^+$  and a hydroxyl ion is changed to  $\text{H}_2\text{O}$ , preserving the balance of charge. Such a change is permitted by the size of the water molecule. In karpfossiderite the formula could be written as  $\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ , the potassium positions remaining vacant. Similarly the minerals listed as acid phosphates by Schaller, namely, hamlinite, plumbogummite, gorceixite etc., and harttite are probably related to the above compounds. For example, plumbogummite probably is  $\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ , which is related to jarosite by replacement of  $\text{K}^+$  by  $\text{Pb}^{++}$ ,  $\text{SO}_4^{--}$  by  $\text{PO}_4^{---}$  and  $\text{OH}^-$  by  $\text{H}_2\text{O}$  neutral. In all of these minerals hydroxyl is probably statistically replaced by water and the crystal symmetry is retained.

A particular mineral has the possibility of showing any of the various types of replacement. Thus plumbojarosite might show variation toward corkite, plumbogummite, or a hydrous form in which the vacant positions are filled with water.<sup>15</sup> There is no explanation in the structure for the observation that the various minerals are usually found free of extensive isomorphous replacement.

Powder photographs of the alunite ores from Marysvale, Utah, all showed diffraction lines of quartz. The intensity variation of the quartz pattern was, moreover, that to be expected from the  $\text{SiO}_2$  content of the samples. It would seem therefore that the silica is present as a separate very finely divided crystalline phase. Alunite has also been shown to occur associated with halloysite  $(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O})$ <sup>16</sup> and more commonly with diasporite  $(\text{AlO}(\text{OH}))$ . These observations indicate that alunite does not form appreciable solid solutions containing excess  $\text{Al}^{+++}$ , i.e. replacing  $\text{K}^+$ , in which  $\text{SiO}_4$  replaces  $\text{SO}_4$ . This is to be expected from the structure, but introduction of some  $\text{SiO}_4$  as a replacement of  $\text{SO}_4$  with accompanying substitution of something like  $\text{Ca}^{++}$  for  $\text{K}^+$  might be possible.

<sup>15</sup> Mr. E. P. Henderson of the U. S. National Museum has given permission to quote some unpublished results obtained by him while working with the U. S. Geological Survey. "Upon measuring the loss on ignition in presence of  $\text{PbO}$  of several samples of plumbojarosites one was found in which the loss was 12.70% at  $600^\circ$  and even at  $450^\circ$  had lost 11.09% (calculated per cent of water in plumbojarosite is 9.57)." It might be suggested that if this loss is truly due to water then replacements of the type mentioned are probably present.

<sup>16</sup> Ross, C. S. and Kerr, P. F. *Professional Paper 1856*, U. S. Dept. of Interior, p. 135-148.

## SUMMARY

X-ray diffraction data have been obtained from alunite, jarosite, natro-, argento-, ammonio- and plumbojarosites, karphosiderite, borgströmite, hamlinite, and the compound  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ . The crystal structure of the alunite-jarosite group of minerals is derived from these data and an explanation is advanced for the various types of isomorphous replacements shown by the group. These structures are characterized by binding between hydroxyl groups and an oxygen atom of a sulfate group.



## BRAUNITE FROM MASON COUNTY, TEXAS\*

D. F. HEWETT AND W. T. SCHALLER, *U. S. Geological Survey.*

The Spiller manganese mine, 15 miles northeast of Mason, Mason County, Texas, was hastily examined by one of the authors (D. F. H.) in May 1934, and subsequent study of the ores has shown that the principal manganese mineral is braunite, which appears to be rare in the United States.

Explorations at the Spiller mine include several open cuts, tunnels, and shafts, which are largely confined to an area about 100 by 600 feet along the crest of a ridge. The deposit was explored in a small way during the war but most of the workings were apparently made prior to 1891.<sup>1</sup> At that time, it was stated "The ore is a hard, steel-gray oxide, blending into a softer, fine-grained crystalline oxide." The presence of garnet (spessartite?) was also noted. This examination confirms the essentials of the description of the local geology as given by Penrose.

The prevailing rock of the explored area is quartzite, which in places contains enough microcline to be regarded as a gneiss. It is a part of the Valley Spring gneiss<sup>2</sup> of the Archean system. This is cut by a few dikes of coarse pegmatite, 5 to 15 inches wide, and by numerous quartz veins as much as 40 inches wide. The laminations of the quartzite trend generally northeast and dip at low angles northwest. They reveal gentle folds but are not plicated. Grains of garnet are distributed in layers in the quartzite but locally also form solid lenses. Tests by Miss J. J. Glass of the United States Geological Survey show that the index of refraction of this garnet is 1.803 and that it is probably a mixture of almandite and spessartite.

The principal manganese mineral is braunite, which is black with sub-metallic luster on polished surfaces. It is the principal constituent of the lenses that have been mined and shipped. One of these attains a maximum width of 3 feet and has been explored horizontally about 75 feet. It lies parallel to the lamination of the quartzite.

The common oxides of manganese, such as pyrolusite, manganite, psilomelane, and wad, seem to be conspicuously absent. As the principal manganese mineral is braunite, with garnet and albite as accessories, the deposit is unique in the United States. It resembles some of the Indian deposits which Fermor has described.<sup>3</sup>

\* Published by permission of the Director, United States Geological Survey.

<sup>1</sup> Penrose, R. A. F., Manganese, its ores, uses, deposits: *Geol. Survey Arkansas*, vol. 1, pp. 442-443, 1891.

<sup>2</sup> Sellards, E. H., Adkins, W. S., and Plummer, F. B., The geology of Texas, vol. 1, *Stratigraphy: Univ. Texas Bull.* 3232, pp. 30-37, 1932.

<sup>3</sup> Fermor, L. L., The manganese-ore deposits of India: *Geol. Survey India, Memoir* 37, Pt. 1, Mineralogy, pp. 52-78, 1909.

In the opinion of the authors, the assemblage of minerals indicates that the deposit has been formed by hydrothermal processes at great depth.

The ore from the Spiller mine varies in texture from a fine-grained compact mass to a coarser aggregate with imperfect crystals up to a centimeter long. Massive cleavable albite (about 95 Ab), garnet, and thin seams of reddish-brown earthy hematite are the only associated minerals noted on the hand specimen.

Three polished surfaces were made and examined by reflected light by Charles F. Park, Jr., of the United States Geological Survey. One was from the same piece from which the material analyzed was obtained, the other two were from different parts of a larger specimen. All three polished surfaces show that neither hematite nor magnetite is present. One surface shows small isolated swarms of an unidentified whitish mineral, probably tetragonal, and strongly anisotropic, which effervesces with  $\text{H}_2\text{O}_2$  without etching. It was not observed in the material analyzed and in the other specimen was present to the extent of a few per cent only.

The braunite is cut by a network of tiny veinlets of hausmannite showing typical twinning and very strong anisotropism. Hausmannite is estimated to be present to the extent of 5 to 10 per cent of the material, and is, in turn, veined by and appears to be altering to a soft gray undetermined mineral. The braunite also contains remnants of an unknown mineral of about the same hardness as braunite and a little darker gray in color. This unknown mineral is isotropic and reacts negatively to  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{KCN}$ ,  $\text{KOH}$ ,  $\text{FeCl}_3$ ,  $\text{SnCl}_2$ ,  $\text{HgCl}_2$ , and  $\text{H}_2\text{O}_2$ .

The chemical analysis and goniometric measurements of the crystals by Schaller identify the black mineral as braunite. Both the color and streak of the Spiller braunite are identical with those of known braunites from other localities.

The crystals are typically octahedral in habit with smaller faces of four other forms, one of which is new for braunite. The usual orientation of braunite (Haidinger, Dana), with  $c=0.9850$ , makes the perfect cleavage form the pyramid of the first order  $\{111\}$ . Goldschmidt turns the crystals  $45^\circ$  and makes the perfect cleavage form the pyramid of the second order  $\{011\}$ , with  $c=1.4032$ . Goldschmidt's orientation yields simpler indices and shows the isozonal relation of the pyramids better than the more generally adopted orientation.

The measured forms and angles are given in the following table, the angles being given in Goldschmidt's orientation.

## FORMS AND ANGLES OF BRAUNITE FROM THE SPILLER MINE, MASON COUNTY, TEXAS

Forms		Description	Measured		Calculated	
Dana	Goldschmidt		$\phi$	$\rho$	$\phi$	$\rho$
$c\{001\}$	$c\{001\}$	Small, square	.....	0 00	.....	0 00
$p\{111\}$	$e\{011\}$	Large, dominant	0 04	54 35	0 00	54 31
$*D\{867\}$	$*D\{177\}$	Small, narrow	8 03	54 49	8 08	54 47
$\sigma\{645\}$	$\sigma\{155\}$	Medium	11 21	55 21	11 18	55 03
$\gamma\{423\}$	$\gamma\{133\}$	Medium	18 17	55 54	18 26	55 56

The form  $*D\{867\}$ , Dana, or  $*D\{177\}$ , Goldschmidt, is new for braunite. It is present on a portion of a crystal as two small narrow faces, broader than line faces but narrower than the faces of  $\sigma$  and  $\gamma$ . The average of repeated measurements is given above.

The form lies in the zone

(201).....(111) Dana  
or (111).....(011) Goldschmidt

The forms of braunite in the zone segment (011)...(111), Goldschmidt, are:

Forms	$e$	$*D$	$\sigma$	$\gamma$	$v$	$f$	$d$
	011	177	155	133	122	344	111
$p =$	0	$\frac{1}{7}$	$\frac{1}{5}$	$\frac{1}{3}$	$\frac{1}{2}$	$\frac{3}{4}$	1
$v/1-v =$	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{3}$	1	3	$\infty$
$2v =$	0	$\frac{1}{2}$	$\frac{1}{2}$	1	2	(6)	$\infty$
$N_3 =$	0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	1	$\frac{3}{2}$	$\infty$

The new form  $D\{177\}$  fits perfectly in the normal series  $N_3$ .

## ANALYSIS OF BRAUNITE FROM THE SPILLER MINE, MASON COUNTY, TEXAS

	Analysis	Analysis <sup>a</sup> recalculated	Calculated 81 per cent $3\text{Mn}_2\text{O}_3$ · $\text{MnSiO}_3$ 19 per cent $3\text{Fe}_2\text{O}_3$ · $\text{MnSiO}_3$
$\text{SiO}_2^b$	9.90	10.01	9.93
$\text{MnO}$	66.89	68.03	68.72
$\text{Fe}_2\text{O}_3$	15.39	15.57	14.92
$\text{O}$	6.27	6.34	6.43
$\text{CaO}$	0.06	—	—
$\text{MgO}$	0.19	—	—
$\text{H}_2\text{O}$	0.73	—	—
Insoluble gangue	0.67	—	—
	100.10	100.00	100.00
Sp. gr. = 4.729			

<sup>a</sup> Recalculated to 100 per cent after changing  $\text{CaO}$  and  $\text{MgO}$  to their equivalent of  $\text{MnO}$  and deducting  $\text{H}_2\text{O}$  and insoluble gangue.

<sup>b</sup> Soluble silica.



The analysis of the braunite is given above with a comparison of the composition of an isomorphous mixture of the two molecules  $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_2$ , and  $3\text{Fe}_2\text{O}_3 \cdot \text{MnSiO}_3$ , in the percentages shown, the analysis showing that a considerable quantity of ferric oxide,  $\text{Fe}_2\text{O}_3$ , is present in the mineral.

The analysis can also be stated in another form by combining the available oxygen (given as 6.34 per cent O in the recalculated analysis) with enough MnO to form  $\text{Mn}_2\text{O}_3$ , the remaining MnO then being combined with the  $\text{SiO}_2$  to form  $\text{MnSiO}_3$ .

#### ANALYSIS OF BRAUNITE STATED IN ANOTHER FORM

	Recalculated analysis	Calculated 81 per cent $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$ 19 per cent $3\text{Fe}_2\text{O}_3 \cdot \text{MnSiO}_3$
$\text{SiO}_2$ .....	10.01	9.93
$\text{MnO}$ .....	11.90	11.70
$\text{Mn}_2\text{O}_3$ .....	62.52	63.45
$\text{Fe}_2\text{O}_3$ .....	15.57	14.92
	<hr/> 100.00	<hr/> 100.00

That the  $\text{Fe}_2\text{O}_3$  is an essential part of the braunite and is not due to enclosed hematite, or other iron mineral, is shown by a consideration of the molecular ratios calculated from the above analysis.

The ratios are:

$\text{SiO}_2$ .....	0.1666	or	1.01
$\text{MnO}$ .....	0.1678	or	1.01
$\text{Mn}_2\text{O}_3$ .....	0.3959	or	2.39
$\text{Fe}_2\text{O}_3$ .....	0.0975	or	0.59
			} 2.98

The formula for braunite is  $\text{SiO}_2 \cdot \text{MnO} \cdot 3(\text{Mn}, \text{Fe})_2\text{O}_3$  and all the iron has to be added to the manganic manganese to yield the ratio of 1:1:3, as required by the formula. The absence of hematite, or other iron oxide, was also proven by the examination of three polished surfaces by reflected light.

The presence of hausmannite,  $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ , and the other undetermined, probably manganese, minerals, would tend to raise slightly the ferric oxide content of the braunite itself. The content of  $\text{SiO}_2$  is so close to the calculated value and the ratios of  $\text{SiO}_2 : \text{MnO} : (\text{Mn}, \text{Fe})_2\text{O}_3$  are so close to 1:1:3, as to suggest that the material analyzed contained less than the estimated 5–10 per cent of hausmannite, as indicated by Park's study of the polished surfaces of the ore.

The consideration of the isomorphous replacement of  $\text{Mn}_2\text{O}_3$  by  $\text{Fe}_2\text{O}_3$  in braunite is confirmed by the work of Zachariasen,<sup>4</sup> and Pauling and Shappell<sup>5</sup> on bixbyite, their conclusion being that the formula of bixbyite should be written  $(\text{Mn}, \text{Fe})_2\text{O}_3$ . The formula of the Spiller braunite may then be more accurately written  $3(\text{Mn}, \text{Fe})_2\text{O}_3 \cdot \text{MnSiO}_3$  or, as  $\text{Fe}_2\text{O}_3$  is not an essential constituent of all braunites, and the simpler formula  $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$  is usually taken as that of braunite in general, the Spiller braunite may be defined as a ferrian braunite, using the descriptive form suggested by one of us.<sup>6</sup>

The isomorphous relation of  $\text{Mn}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in braunite and bixbyite and in other minerals (the epidote series, purpurite-heterosite, etc.) makes it seem doubtful if their separation in a formula, with definite ratio, is valid, and casts suspicion on such a formula, for example, as is given for sitaparite, namely  $9\text{Mn}_2\text{O}_3 \cdot 4\text{Fe}_2\text{O}_3 \cdot \text{MnO}_2 \cdot 3\text{CaO}$ , and beldongrite, namely  $6\text{Mn}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{MnO}_2 \cdot 8\text{H}_2\text{O}$ . Vredenburgite, with a supposed formula  $3\text{MnO} \cdot 3\text{Mn}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3$ , has been shown<sup>7</sup> to be a mixture of jacobsite,  $\text{MnO} \cdot \text{Fe}_2\text{O}_3$ , and hausmannite,  $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ , and, in the type specimen, with still other manganese minerals.

The Spiller braunite seems to contain the highest reported percentage of  $\text{Fe}_2\text{O}_3$ , namely 15.39, although two other analyses approach this figure closely, namely one of braunite from the Engadine, Switzerland, with 14.55 per cent<sup>8</sup>  $\text{Fe}_2\text{O}_3$ , and another from India with 14.14 per cent<sup>9</sup>  $\text{Fe}_2\text{O}_3$ . Doelter<sup>10</sup> lists six additional analyses of braunite with  $\text{Fe}_2\text{O}_3$  ranging from 11.40 to 12.91 per cent, although there is no assurance for some of the older analyses that the reported  $\text{Fe}_2\text{O}_3$  was not due to impurities.

<sup>4</sup> Zachariasen, William, Über die Kristallstruktur von Bixbyite, sowie vom künstlichen  $\text{Mn}_2\text{O}_3$ : *Zeits. Krist.*, vol. 67, pp. 455-464. 1928.

<sup>5</sup> Pauling, Linus, and Shappell, M. D., The crystal structure of bixbyite and the C-modification of the sesquioxides: *Zeits. Krist.*, vol. 75, pp. 128-142, 1930.

<sup>6</sup> Schaller, W. T., Adjectival ending of chemical elements used as modifiers to mineral names: *Am. Mineral.*, vol. 15, pp. 566-574, 1930.

<sup>7</sup> Dunn, J. A., A study of some microscopical aspects of Indian manganese-ores: *Trans. National Inst. Sciences India*, vol. 1 (no. 7), pp. 103-124. 1936.

<sup>8</sup> Bukeyen, Fried., Mineral-Analysen. z. Braunite: *Sitzungsber. Akad. Wissensch. Wien*, vol. 24, p. 287, 1857.

<sup>9</sup> Fermor, L. L., The manganese-ore deposits of India: *Geol. Survey India, Mem.* 37, p. 68, 1909.

<sup>10</sup> Doelter, Cornelius, *Handb. d. Mineralchemie*, vol. 3, pt. 2, pp. 896-899, 1926.

## CHALCOMENITE FROM BOLIVIA

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### SUMMARY

Good crystals of chalcomenite— $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$  from a new locality, Hiaco mine, Pacaake, about 30 km. ENE. of Colquichaca, Bolivia, are orthorhombic, disphenoidal;  $a:b:c=0.7325:1:0.8077$ , in agreement with the form of the artificial salt. Forms:  $\ast c\{001\}$ ,  $\ast b\{010\}$ ,  $n\{120\}$ ,  $m\{110\}$ ,  $q\{011\}$ ,  $d\{101\}$ ,  $o\{111\}$ ,  $p\{\bar{1}11\}$ ,  $\delta\{141\}$ . Structure cell: simple orthorhombic; class 2 2 2; space group  $P 2_1 2_1 2_1$ ;  $a_0=6.65$ ,  $b_0=9.10$ ,  $c_0=7.36 \text{ \AA}$ ;  $a_0:b_0:c_0=0.731:1:0.809$ ; contains  $\text{Cu}_4\text{Se}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$ . Cleavage none; H slightly over 2;  $G=3.35$ . Crystals clear blue, transparent, pleochroic.  $X$  (light blue)  $=a[100]$ ,  $Y$  (darker blue)  $=c[001]$ ,  $Z$  (darker blue)  $=b[010]$ . Indices (Na):  $nX=1.712$ ,  $nY=1.732$ ,  $nZ=1.732$ , all  $\pm 0.002$ . Negative;  $2V$  nearly zero;  $r < v$ , strong.

Chalcomenite, a hydrous selenite of copper from Cerro de Cacheuta in the Argentine, was named by Des Cloizeaux and Damour (1881), who described the crystals as monoclinic. In a separate communication Damour (1881) gave an analysis of the new mineral and derived the composition  $\text{CuO} \cdot \text{SeO}_2 \cdot 2\text{H}_2\text{O}$ . Friedel and Sarasin (1881 A) succeeded in preparing large crystals of the same composition; these were found by the same authors (1881 B) to be orthorhombic, and apparently unlike the natural salt in form. These papers remain after more than fifty years the sole source of information concerning this uncommon mineral.

Chalcomenite has now been determined among the oxidation products of the nickel-copper selenide, blockite, recently described by Herzenberg and Ahlfeld (1935)<sup>1</sup>; a study of this new occurrence permits a revision and extension of our knowledge of the older species. The specimens studied were sent to the Harvard Mineralogical Museum by Dr. Ahlfeld; they came from the lead-silver mine, Hiaco, in Pacaake, about 30 kilometers ENE. of Colquichaca, Bolivia. Herzenberg and Ahlfeld mention a number of oxidation products associated with blockite, including white needles of what they took to be selenolite and a red mineral regarded as new and named ahlfeldite, but later recognized as cobaltomenite. It is hoped that better material will come to hand which will enable these little-known minerals to be exactly described.

On the few small specimens available, consisting mostly of blockite, there are various acicular white minerals, one of which could be identified as cerussite; molybdomenite is probably among them and cobaltomenite is also present in several druses. Chalcomenite, with the charac-

<sup>1</sup> Since this paper went to press blockite has been identified with penroseite by Banister and Hey (1937).



teristic clear blue color, appears in cavities lined with limonite, together with the minerals already mentioned, or quite alone. The largest crystal seen is not more than 3 mm. in greatest dimension. The common habit is acicular, the needles measuring but a fraction of a millimeter in diameter. Despite their minute size, the crystals gave fairly consistent measurements.

*Crystallography.* The new crystals of chalcomenite were measured and projected with reference to the axis of acicular development. The resulting projections showed a vertical axis of two-fold symmetry, which was also clearly expressed by the development of the faces, but no vertical plane of symmetry. The crystals thus appeared to be monoclinic, elongated with the symmetry axis; and it was easy to choose elements leading to a notable simplification of the complex indices of Des Cloizeaux and Damour.

Optical study by Dr. Berman showed, however, that the principal optical directions coincide with possible orthorhombic crystal axes; while an  $x$ -ray study, also by Dr. Berman, proved the presence of two rectangular axes of two-fold symmetry perpendicular to the needle axis. These observations indicated that the crystals are orthorhombic-disphenoidal rather than monoclinic. Taking the needle axis as the vertical axis, the simplest choice of orthorhombic elements, which were found to agree with the elements of the structural lattice, gave values that correspond closely with those of Friedel and Sarasin when the axes of these authors are suitably interchanged.

One difficulty remained, however. Opposite ends of a disphenoidal crystal present the same aspect while the terminations at opposite ends of the symmetry axis of a monoclinic crystal are in right- and left-hand relation. Doubly terminated crystals were not found; but both right- and left-hand projections were obtained from the singly terminated crystals. This fact may be explained in three ways: (1) the crystals are monoclinic with rectangular axes; (2) they are disphenoidal with hypothetical twinning on (001); (3) they are disphenoidal with the unit disphenoids in right-hand  $\{111\}$  and left-hand  $\{\bar{1}\bar{1}1\}$  positions equally common, never occurring together, and not distinguishable. Of these three possibilities the last appears to be the most probable.

Table 1 gives the forms and measured angles obtained from crystals of chalcomenite. The best measurements lead to the elements:  $a:b:c = 0.7325:1:0.8077$  which agree well with the ratio:  $a:c:b = 0.7358:1:0.8111$ , computed from Friedel's and Sarasin's measurements on the artificial salt.

TABLE 1. CHALCOMENITE: TWO-CIRCLE MEASUREMENTS

Form	Mean		Range		No. of faces	Quality
	$\phi$	$\rho$	$\phi$	$\rho$		
* <i>c</i> 001	—	0°00'	—	—	4	good
* <i>b</i> 010	0°00'	90 00	0°02'– 0°10'	—	2	very poor
<i>n</i> 120	35 36	90 00	34 50–36 22	—	19	very poor
<i>m</i> 110	53 54	90 00	53 31–54 03	—	9	very good
<i>q</i> 011	0 00	38 51	0 01– 0 10	38°40'–38°59'	3	very good
<i>d</i> 101	90 00	47 50	89 46–90 19	47 33–48 00	10	very good
<i>o</i> 111 <i>p</i> $\overline{1}11$	± 53 47	53 44	± 53 05–54 27	53 32–54 00	5	poor
$\delta$ 141	15 50	73 17	14 42–16 57	72 35–74 00	2	very poor

\* New form.

In the presentation of the crystallography of chalcomenite, Dana (1892) followed Des Cloizeaux and Damour. Goldschmidt (1897; 1912) took the same axial directions but changed the parametral lengths to obtain some simplification of indices. Groth (1908) reproduced the data of Friedel and Sarasin on the artificial compound. In Table 2 the several settings are correlated by the appropriate transformation formulas and by tabulation of the corresponding form letters and symbols.

TABLE 2. CHALCOMENITE: CORRELATION OF FORMS

Des Cloizeaux & Damour (Dana) to Palache:  $10\overline{2}/104/010$ Goldschmidt to Palache:  $20\overline{1}/202/020$ Friedel & Sarasin (Groth) to Palache:  $100/001/010$ 

Des C. & Damour	Dana	Goldschmidt	Friedel & Sarasin	Groth	Palache
—	—	—	—	—	<i>c</i> {001}
—	—	—	—	—	<i>b</i> {010}
<i>p</i> {001}	<i>c</i>	<i>a</i> {001}	$a^2$ {102}	<i>s</i>	<i>n</i> {120}
<i>o</i> $\frac{1}{2}$ {801}	<i>f</i>	<i>f</i> {201}			
<i>h</i> <sup>1</sup> {100}	<i>a</i>	<i>c</i> {100}	$a^1$ {101}	<i>r</i>	<i>m</i> {110}
$a^1$ {101}	<i>g</i>	<i>g</i> {104}			
$\beta$ {2.12.1}	$\beta$	$\beta$ {162}	—	—	$\beta$ {012}
$\epsilon$ {261}	$\epsilon$	$\epsilon$ {132}	$e^1$ {011}	<i>q</i>	<i>q</i> {011}
—	—	—	$e^2$ {012}	<i>t</i>	<i>t</i> {021}
—	—	—	<i>m</i> {110}	<i>m</i>	<i>d</i> {101}
<i>m</i> {110}	<i>m</i>	<i>m</i> {110}	$b^{1/2}$ {111}	<i>o</i>	<i>o</i> {111}
$\delta$ {421}	$\delta$	$\delta$ {212}	—	—	<i>p</i> { $\overline{1}11$ }
					$\delta$ {141}

Table 3 compares the fundamental angles of the earlier authors with the new values. The agreement with the values for the artificial salt (Friedel & Sarasin) is very good; the previous measurements on the natural mineral, obtained from poorly developed crystals, accord less well with the new angles.

TABLE 3. CHALCOMENITE: INTERFACIAL ANGLES

Des Cloizeaux & Damour	Friedel & Sarasin	Palache
$m\ h^1 = 35^\circ 50'$	—	$om = 36^\circ 11\frac{1}{2}'$
$p\ a^1 = 18\ 54$	$a^2a^1 = 19^\circ 27\frac{1}{2}'$	$nm = 19\ 27\frac{1}{2}$
$a^1h^1 = 71\ 57$	$a^1a^1 = 72\ 41\frac{1}{2}$	$mm = 72\ 27$
—	$m\ m = 84\ 25\frac{1}{2}$	$dd = 84\ 25$

Table 4 is an angle-table for chalcocite in the adopted setting.

TABLE 4. CHALCOMENITE— $\text{CuSeO}_8 \cdot 2\text{H}_2\text{O}$ 

Orthorhombic; disphenoidal—2 2 2

$a:b:c = 0.7325:1:0.8077$        $p_0:q_0:r_0 = 1.1026:0.8077:1$   
 $q_1:r_1:p_1 = 0.7325:0.9070:1$        $r_2:p_2:q_2 = 1.2381:1.3651:1$

Forms	$\phi$	$\rho = C$	$\phi_1$	$\rho_1 = A$	$\phi_2$	$\rho_2 = B$
$c\ 001$	—	$0^\circ 00'$	$0^\circ 00'$	$90^\circ 00'$	$90^\circ 00'$	$90^\circ 00'$
$b\ 010$	$0^\circ 00'$	$90\ 00$	$90\ 00$	$90\ 00$	—	$0\ 00$
$n\ 120$	$34\ 19$	$90\ 00$	$90\ 00$	$55\ 41$	$0\ 00$	$34\ 19$
$m\ 110$	$53\ 46\frac{1}{2}$	$90\ 00$	$90\ 00$	$36\ 13\frac{1}{2}$	$0\ 00$	$53\ 46\frac{1}{2}$
$\beta\ 012$	$0\ 00$	$21\ 59\frac{1}{2}$	$21\ 59\frac{1}{2}$	$90\ 00$	$90\ 00$	$68\ 00\frac{1}{2}$
$q\ 011$	$0\ 00$	$38\ 55\frac{1}{2}$	$38\ 55\frac{1}{2}$	$90\ 00$	$90\ 00$	$51\ 04\frac{1}{2}$
$t\ 021$	$0\ 00$	$58\ 14\frac{1}{2}$	$58\ 14\frac{1}{2}$	$90\ 00$	$90\ 00$	$31\ 45\frac{1}{2}$
$d\ 101$	$90\ 00$	$47\ 47\frac{1}{2}$	$0\ 00$	$42\ 12\frac{1}{2}$	$42\ 12\frac{1}{2}$	$90\ 00$
$o\ 111$	$53\ 46\frac{1}{2}$	$53\ 48\frac{1}{2}$	$38\ 55$	$49\ 22\frac{1}{2}$	$42\ 12\frac{1}{2}$	$61\ 31$
$p\ 111$	$-53\ 46\frac{1}{2}$	$53\ 48\frac{1}{2}$	$-126\ 13\frac{1}{2}$	$49\ 22\frac{1}{2}$	$137\ 47\frac{1}{2}$	$61\ 31$
$\delta\ 141$	$18\ 50\frac{1}{2}$	$73\ 40\frac{1}{2}$	$72\ 48$	$71\ 56\frac{1}{2}$	$42\ 12\frac{1}{2}$	$24\ 44$

*X-ray measurements.* The following photographs were made on a small crystal of chalcocite, using copper radiation: rotation, equator Weissenberg and first layer Weissenberg about  $c[001]$ ; and an equator Weissenberg about  $b[010]$ . These photographs confirm the orthorhombic symmetry and show that the mineral has a simple lattice with the cell dimensions:





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## IDENTIFICATION OF CERTAIN GEM-STONE MATERIALS BY THEIR EMISSION SPECTRA

DAVID H. HOWELL, *Pasadena, California.*

The application of petrographic methods, using thin sections and mineral fragments, for the identification of mineral species, frequently cannot be carried out with cut and polished gem-stone materials. The examination of this type of material must be conducted without serious damage to the specimen, and thus gemological tests are sometimes handicapped when the physical and optical data are insufficient to identify the species conclusively. This investigation was prompted by failure to identify a certain red gem-stone weighing 22.37 carats with a value of 1.716 for its index of refraction and 3.61 for its gravity. Absorption bands in the visible region,<sup>1</sup> indicative of pyrope, were observed using a Gaertner spectroscope. Since this index is possible for both garnet<sup>2</sup> and spinel<sup>2,3</sup> and the density may be a value of either mineral,<sup>2,3,4</sup> more information was required to definitely identify the specimen. Spectrograms were obtained of this stone, designated as sample No. 1, also of two spinels, samples No. 2 and 3, and of a garnet, sample No. 4. The examination was subsequently extended to specimens of tourmaline, andalusite, jadeite, nephrite, fibrolite and epidote. Kunz<sup>5</sup> states, "Sausurite is probably the most important of these materials easily mistaken for true jade. It is a compact, tough, heavy mineral with a hardness and gravity almost identical with jadeite, and this makes the differentiation difficult." He places fibrolite second in the list of minerals difficult of separation from jadeite and says, "... it is readily identified chemically being a practically pure silicate of aluminum." Others also give these minerals as difficult to identify.<sup>6</sup> Andalusite and tourmaline may like-

<sup>1</sup> These figures were given by R. M. Shipley, Jr., of the Gemological Institute of America, Los Angeles, Calif., whose idea prompted the initial experiment with garnet and spinel.

<sup>2</sup> Eppler, W. F., *Edelsteine und Schmucksteine*, Leipzig, 1934, p. 266 and p. 310.

*Dana's Textbook of Mineralogy*, 4th Edition, revised by Ford, 1932, pp. 592-594 and p. 488.

Kraus and Holden, *Gems and Gem Materials*, 1931, pp. 238-239 and pp. 246-247.

Winchell, A. N., *Elements of Optical Mineralogy*, 1933, pp. 176-177 and p. 62.

Spencer, L. J., *A Key to Precious Stones*, Glasgow, 1936, p. 186 and p. 167.

<sup>3</sup> Bauer, Max, *Edelsteinkunde*, 3rd Edition, revised by Karl Schlossmacher, Leipzig, 1932, p. 549.

<sup>4</sup> Chuboda, Karl, *The Gemmologist*, vol. 5, pp. 267-270, 1936. Bauer, Max, *ibid.*, p. 549 and p. 566.

<sup>5</sup> Kunz, G. F., *Encyclopaedia Britannica*, 14th Edition, 1929, vol. 12, p. 864.

<sup>6</sup> Bauer, Max, *ibid.*, pp. 650-652. Doelter, C., *Handb. Mineralchemie*, II, Pt. 1, p. 694, 1914.

wise be confused.<sup>7</sup> Ford<sup>8</sup> states that zoisite "includes the essential part of the mineral material known as saussurite (e.g., in saussurite-gabbro), which has arisen from the alteration of feldspar." Due to inability to obtain specimens of saussurite or zoisite, epidote was substituted and examined.

#### PREPARATION AND EXAMINATION OF SAMPLES

The samples of garnet and spinel for spectrographic study were removed from the fashioned gems by careful application of a corundum hardness point to one of the back facets of each stone, close to the girdle. The material abraded was deposited directly upon the spectrographic electrodes, and weighed approximately 0.1 mg. A slightly rounded point was found to be better for removing the samples than a sharp one as sufficient material was procured without cutting too deeply into the specimen.

The extension of this first work was conducted with samples obtained as just stated. However, a carborundum point was employed instead of corundum. The quantity used, in each case, was of the same magnitude. The aluminum contamination from the corundum point was not deemed serious in the garnet-spinel examination since silicon was to be the element of interest in showing the compositional differences between these two minerals. Silicon was expected to be present in the examinations in all the other minerals and thus very slight contaminations from the silicon carbide were not deemed serious. However, the use of a diamond point is recommended for this type of investigation. The spectrographic technique and the interpretation of the plates have been previously described.<sup>9</sup>

TABLE OF RESULTS

Sample Number	Large	Medium	Small	Very Small
Sample—No. 1	Mg Al	—	—	—
Spinel—No. 2	Mg Al	—	—	—
Spinel—No. 3	Mg Al	—	—	—
Garnet—No. 4	Mg Si Al	Fe Mn	—	—

<sup>7</sup> Bauer, Max, *ibid.*, p. 615. Eppler, W. F., *ibid.*, p. 277.

<sup>8</sup> Dana's *Textbook of Mineralogy*, *ibid.*, p. 621.

<sup>9</sup> Kennard, T. G., and Howell, D. H., *Am. Mineral.*, vol. 21, pp. 721-726, 1936.

TABLE OF RESULTS (*Continued*)

Sample Number	Large	Medium	Small	Very Small
Jadeite—No. 1	Si	Al	—	Mg
Jadeite—No. 2	Si (Na)*	Al (Ca)	—	Mg
Jadeite—No. 3	Si	Al	—	Mg
Nephrite—No. 1	Mg Si	—	—	Al
Nephrite—No. 2	Mg Si	—	—	Al (Ca)
Nephrite—No. 3	Mg Si	—	—	Al
Epidote—No. 1	Si Al	Fe (Ca)	—	Mg
Epidote—No. 2	Si Al	Fe	—	Mg
Epidote—No. 3	Si Al	Fe	—	Mg
Sillimanite—No. 1	Si Al	—	—	Fe (Na) (Ca)
Sillimanite—No. 2	Si Al	—	—	Fe
Tourmaline—No. 1	Si Al	B	—	Fe Mn Mg
Tourmaline—No. 2	Si Al	B	—	Fe Mn Mg
Tourmaline—No. 3	Si Al	B	—	Fe Mn Mg



TABLE OF RESULTS (*Continued*)

Sample Number	Large	Medium	Small	Very Small
Andalusite—No. 1	Si Al	—	—	Fe Mg
Andalusite—No. 2	Si Al	—	—	Fe Mg
Andalusite—No. 3	Si Al	—	—	Fe Mg

\* The elements which are enclosed in brackets were recorded in the visible region.

Due to the technique employed and the very small quantity of material composing the spectrographic samples, traces of impurities are not recorded in the table of results.

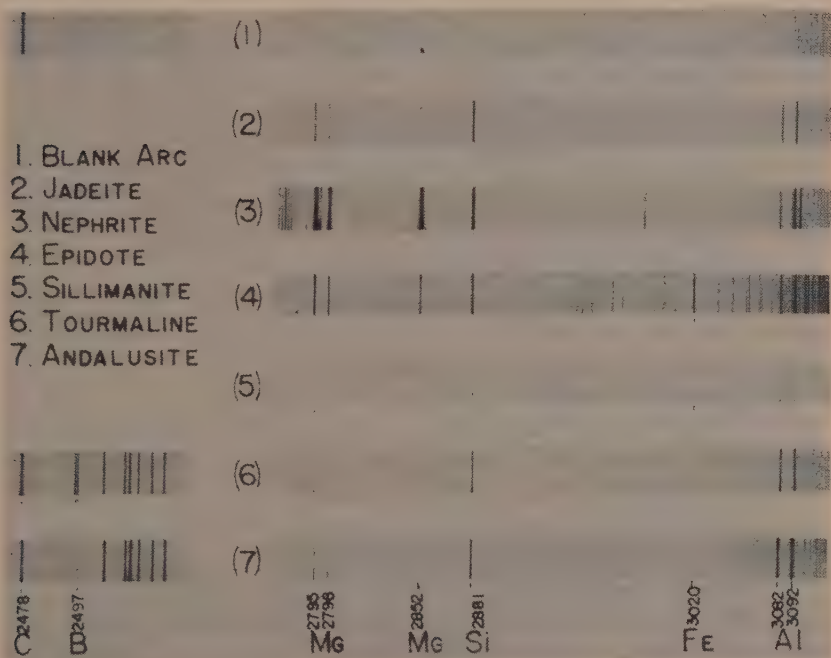


FIG. 1

## DISCUSSION OF RESULTS

The spectrum of sample No. 1 in the first group showed the presence of magnesium and aluminum with traces of silicon. This agreed with the spectra of two known spinels. Comparison of the spectra of sample No. 1 and sample No. 4, a garnet, showed a marked dissimilarity in composition. Thus, though the gravity and refractive index were insufficient to determine the gem's identity, spectroscopy showed the chemical composition of sample No. 1 to be that of a spinel rather than a garnet.

The spectrographic evidence for sample No. 4 points to a pyralspite garnet.<sup>10</sup> The presence of an appreciable amount of manganese indicates the spessartite variety. Laboratory tests gave the value 1.805 for the index of refraction and 4.05 for gravity which agree for garnets of this variety. The presence of iron and magnesium indicate an admixture of pyrope and almandine molecules.

The spectra produced by jadeite, nephrite and its substitutes are each distinctive. A portion of the spectrum using one sample from each group is reproduced in Fig. 1. The region from 2700Å to 3100Å was found to be satisfactory for establishing significant variations in the silicon, magnesium and aluminum contents. The table of results and the illustration show the silicon comparable in the spectra of jadeite and nephrite, but the aluminum content of the former is greater. In nephrite the reverse is true, for the five magnesium lines between 2777Å and 2783Å appear, indicating a large amount of this element. The aluminum content is approximately that of a trace or a very small amount. This variance in the aluminum, magnesium, silicon ratios is in accordance with the theoretical composition of these minerals.<sup>11</sup>

The spectrum of epidote shows strong iron lines, especially at 3020Å, and this is different from the two preceding spectra. The aluminum, magnesium, silicon ratios in this mineral are definitely not the same as those of either jadeite or nephrite. The intensities of the iron lines are such as to show this element to be present in considerable amount, while in the case of jadeite or nephrite it is present as an impurity in relatively small amount. In a similar manner sillimanite can be separated from jadeite and nephrite. The corresponding tri-element ratios in this aluminum silicate are markedly different.

The tourmaline-andalusite separation is easily made apparent by comparing the strength of the boron lines in the spectrum of each mineral. Tourmaline, a boro-aluminum silicate, gave very strong boron lines while andalusite showed boron to be present only in traces or in very small amounts.

<sup>10</sup> Winchell, A. N., *Elements of Optical Mineralogy*, 1933, vol. II, pp. 174-179.

<sup>11</sup> Doelter, C., *Handb. Mineralchemie*, II, Pt. 1, p. 651. 1914.

The mineral specimens previously sampled as jadeite, No. 2, nephrite, No. 2, epidote, No. 1, and sillimanite, No. 1, were resampled and spectrograms were made in the visible region. These same specimens of jadeite and nephrite were also examined in both the visible and ultra-violet portions of the spectrum, using a very large sample of each, weighing approximately 100 mg. These spectrograms taken in the visible region showed the sodium and calcium content of jadeite, nephrite, epidote and sillimanite. The very large sample of jadeite was of sufficient quantity to produce strong sodium lines at 3302Å. Comparison of the spectral lines of silicon, aluminum, magnesium and iron produced by the very large sample and the minimum samples showed no significant changes in the ratios of these elements but only a diminution of intensity in the small samples. Since analyses of jadeite and nephrite<sup>12</sup> show definitely a great dissimilarity in the aluminum and magnesium contents of these minerals, and since the sensitive spectral lines of these three elements lie in the ultra-violet region, this portion of the spectrum was employed and found satisfactory for differentiation between the ratios of these elements present in each species. The results showed that the identity of a mineral, having the color, physical and optical values possible for either jadeite or nephrite, could be determined by the type of spectrum produced and the tri-element ratios. The sensitive lines of the elements indicating the chemical composition of epidote and sillimanite likewise occur, with the exception of calcium, in the ultra-violet, as do the sensitive boron lines of tourmaline.

The technique just described, employing a very minute amount of a specimen, showed significant differences in the spectra of the specimens examined. These differences in composition may be quantitatively interpreted in terms of specific ratios which definitely separate one species from the other on the basis of chemical composition. The method may be employed to further a positive identification of cut and polished gem-stones, ornamental stones or archaeological artifacts as well as mineral specimens, using less material and causing less damage than is possible with a direct chemical analysis.

#### SUMMARY

(1) A technique is described whereby material sufficient for emission spectroscopy may be obtained without serious damage to valuable specimens.

(2) The method has been tested using specimens of garnet, spinel, jadeite, nephrite, epidote, sillimanite, tourmaline and andalusite and found to be satisfactory in distinguishing between the various species.

<sup>12</sup> Doelter, C., *Handb. Mineralchemie*, II, Pt. 1, pp. 652-680, 1914.

(3) The procedure is considered to be applicable generally in distinguishing between species which have similar optical and physical properties, but different chemical composition.

#### ACKNOWLEDGMENTS

The author wishes to acknowledge the courtesies extended by Pomona College and members of its faculty for the use of laboratories and suggestions, and criticisms regarding these examinations. He wishes to acknowledge in particular the assistance and cooperation of Dr. T. G. Kennard of Claremont Colleges and hereby expresses appreciation for the use of spectrographic equipment which made this work possible.



## NOTES AND NEWS

### HELVITE FROM THE BUTTE DISTRICT, MONTANA\*

D. F. HEWETT†

The rare mineral, helvite ( $3\text{MnBeSiO}_4 \cdot \text{MnS}$ ), was recognized recently by the writer in a specimen from the 200-foot level (west drift) of the Lexington mine, Butte district, Montana, submitted by M. H. Gidel. The workings from which the specimen came are no longer accessible and its associations are unknown. The identification has been confirmed by optical and by spectroscopic tests. So far as the writer can ascertain, this is the third record of the occurrence of this mineral in the United States. For many years it was known only at the Rutherford pegmatite mine, near Amelia Court House, Amelia County, Va.<sup>1</sup> Recently it was identified in material from the Sunnyside mine, San Juan County, Colo.<sup>2</sup>

The specimen, which weighs about four pounds, is largely rhodonite and rhodochrosite, through which sporadic grains of sulphide minerals are scattered. Helvite occurs as sparse lemon-yellow grains as much as 2 mm. in diameter, and as veinlets about 1 mm. wide in the midst of the pink manganese minerals. According to W. T. Schaller, the mineral is isotropic with an index of refraction of 1.734. Spectrographic tests by George Steiger show that it contains considerable beryllium and only a doubtful trace of zinc.

The examination of several polished specimens and thin sections reveals relations of the minerals that are worthy of record. The specimen contains about 75 per cent rhodonite, 15 per cent rhodochrosite, 8 per cent quartz, and 2 per cent of the sulphides, pyrite, galena, and blende. No alabandite was found. The rhodonite forms a felted mass of fine needles which terminate here and there against small rounded masses of rhodochrosite; the carbonate seems to fill the pores of a spongelike mass of silicate and, while the carbonate is the later mineral, it does not replace the silicate. The masses of mixed silicate and carbonate are cut by veinlets that are largely rhodonite in the form of prismatic crystals; here and there the veinlets are filled with quartz, carbonate, or sulphides. In part, the sulphides are disseminated throughout the mass of mixed silicate and carbonate, and a part lies in the later veinlets. In

\* Published by permission of the Director, United States Geological Survey.

† Geologist, United States Geological Survey.

<sup>1</sup> Fontaine, W. M., Notes on the occurrence of certain minerals in Amelia County, Va.: *Am. Jour. Sci.*, vol. 3, no. 25, pp. 330-339, 1883.

<sup>2</sup> Burbank, W. S., The manganese minerals of the Sunnyside veins, Eureka Gulch, Colo.: *Am. Mineral.*, vol. 18, pp. 513-527, 1933.

the examined sections, helvite occurs only in or near the rhodonite veinlets with which sulphides are associated and it was, therefore, one of the last minerals to be deposited.

The paragenetic relations of the minerals in this specimen conform in a broad way with those recorded by Burbank in the material from the Sunnyside mine. This specimen does not show the manganese silicates friedelite, alleghanyite, and tephroite found in the Sunnyside material, but shows the repeated succession of rhodonite-rhodochrosite recorded by Burbank. It seems probable that closer examination of the manganeseiferous veins at Butte will reveal more of the uncommon manganese minerals.

#### CRISTOBALITE AT CRATER LAKE, OREGON

CARL E. DUTTON, *Wayne University, Detroit, Michigan.*

The discussion by Diller and Patton of accessory minerals in the andesites of Crater Lake National Park<sup>1</sup> mentions two occurrences of quartz and one of tridymite. Another mineral, cristobalite, should be added to the list.

The rocks exposed in Crater Lake National Park are in order of abundance andesites, basalts, and dacites. Mt. Mazama, the volcanic ancestor of the present crater, was composed principally of andesites with some later accumulations of dacite. The basalt occurs in adnate cones on the slopes of the former volcano.

In the southwestern corner of the Park, there is a very prominent conical land form known as Union Peak. Diller<sup>2</sup> considers the peak to be composed of andesite lava which solidified in the vent of a tuff cone. The plug was subsequently stripped of its tuff until only remnants now remain.

During a reconnaissance examination of the Union Peak area, an unusual specimen was discovered along the trail on the south side of the Peak. Although it was only a talus fragment, its composition and texture indicated that the mass which contributed the fragment was obviously the rock constituting the Peak. One surface of the talus fragment had dimensions of approximately one by two feet. The designated surface was made conspicuously irregular by the presence of pits or cup-like depressions with diameters from  $\frac{1}{8}$  to  $\frac{1}{2}$  inch and depths of approximately  $\frac{1}{8}$  to  $\frac{1}{4}$  inch.

The surfaces of these pits were covered with small white crystals (Fig. 1) which had the external form of octahedrons and a hardness greater than that of a knife blade. The unfamiliar association of this

<sup>1</sup> Diller, J. S., and Patton, H. H., *U.S.G.S. Prof. Paper* 3, p. 83, 1902.

<sup>2</sup> *Ibid.*, p. 20.

form and hardness resulted in the collection of specimens and later examination by immersion methods. The diagnostic characters of the crystals are general index of refraction of approximately 1.485, pseudo isometric form, and very low interference colors. The mineral was determined as cristobalite, whose occurrence in Crater Lake National Park has not been previously reported. Specimens from the Union Peak locality are now in the museum collections of the Park and of the University of Minnesota.

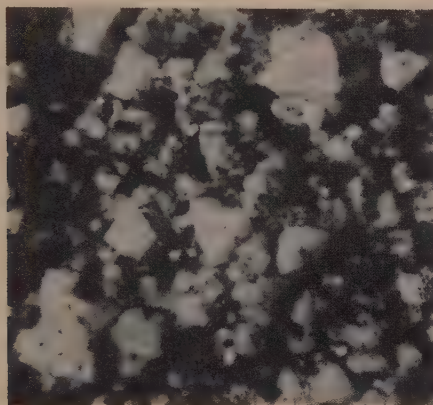


FIG. 1—Photomicrograph of cristobalite crystals ( $\times 12$ ) from Crater Lake National Park, Oregon. Note the skeletal and octahedral forms.

The crystals vary in size from microscopic dimensions to slightly greater than one millimeter. The larger crystals are of sufficient size to permit observation concerning the character of their faces. Most of the faces exhibit a distinct concave form and a few crystals have quadrants so incompletely filled that they are "skeletal" in nature. These characters were also noted in the descriptions of other occurrences.<sup>3</sup> In addition to the skeletal and octahedral habits, aggregates of small crystals are also present.

Associated with the cristobalite crystals are abundant crystals of transparent feldspar (sanidine) and a few crystals of augite. Only very slight amounts of orthoclase were observed in the thin sections of the andesite, and although augite is rather common in the thin sections, it lacks the euhedral forms of the mineral in the cavities. The thin sections of andesite revealed no cristobalite nor other forms of silica.

<sup>3</sup> Rogers, A. F., *Am. Jour. Sci.* (4), vol. 45, pp. 222-226, 1918.

Rogers, A. F., *Am. Mineral.*, vol. 6, pp. 4-6, 1921.

The ridges between the cups are devoid of these crystals and are apparently normal rock surfaces. These conditions imply that the cups are remnants of cavities in which the cristobalite and associated minerals were deposited. This implication is substantiated by the presence of small cavities which lie below the cups but are connected with them by means of constricted openings whose surfaces are covered with small cristobalite crystals. The rock on which these crystals occur is rather dense and shows no evidence of conduits to the cavities. It is possible that such conduits were present in the rock mass containing the other portion of the cavities but no specific evidence as to the method of introduction was observed.

Rogers<sup>4</sup> states that cristobalite is a characteristic mineral of spherulites and that it occurs frequently in cavities. Emmons and Larsen<sup>5</sup> also mention these same conditions of occurrence at Creede, Colorado. In both instances, the cristobalite is considered to have formed in volcanic rocks during the last stages of crystallization, but some occurrences are also possibly the result of conversion by high temperatures. The formation of cristobalite is generally accepted as associated with an abundance of mineralizers and the presence of gas cavities.

As a result of recent studies on the volcanoes of the Cascade Mountains, cristobalite is known to occur abundantly in this area but, except at Crater Lake, only spherulitic forms have been recognized.<sup>6</sup>

<sup>4</sup> Rogers, A. F., *Am. Mineral.*, vol. 13, p. 82, 1928.

<sup>5</sup> Emmons, W. H., and Larsen, E. S., *U.S.G.S. Bulletin* 718, pp. 47-48, 1923.

<sup>6</sup> Williams, Howell, Personal communication. (August 1936).

## PROCEEDINGS OF THE SOCIETIES

### NEW YORK MINERALOGICAL CLUB

The exhibition of the New York Mineralogical Club, celebrating the club's fiftieth year, took place in the Maxwell Hall of the American Museum of Natural History on Saturday afternoon and evening, March 13th. The display was well attended, with over 1100 visitors during the two sessions.

There were several notable exhibits, both among the commercial exhibitors and those of the club members. The Ward exhibit with the new G.E. No. H3 fluorescent lamp and a large number of showy specimens attracted much attention. Bausch and Lomb, and Spencer exhibited the latest models of petrographic apparatus, and Leitz showed photomicrographic equipment. Books were shown by several publishers. An exhibit of changing lights shining up through a specimen of rock crystal, shown by H. T. Strong, served as a center of attraction in the hall. The demonstration by John Vlismas of cutting and polishing objects composed of onyx and fluorite was very instructive for the amateur lapidaries. Microchemical test demonstrations by R. P. Cargille showed the practicability of the technique to many who had never before seen these tests actually made. A new refractometer giving accurate results, used in conjunction with an ordinary microscope, was demonstrated by Lyman Nichols. The instrument is simple, practical and inexpensive, and



has the additional advantage that the higher readings may be made with equal accuracy, beyond the limit of the ordinary Abbe refractometer.

Among the exhibits by the club members were a large number of locally collected specimens from the Paterson and Franklin districts. Some unusual specimens included crystallized greenockite from Paterson, fine crystallized zincite from Franklin, and some unusually excellent crystals of iolite from Guilford, Conn. Mr. F. I. Allen showed what is believed to be a new germanium bearing mineral from Franklin, as well as some fine minerals of the rare earths. Mr. O. I. Lee demonstrated the reversible color changes in hackmanite. A representative of Columbia University projected interference figures and demonstrated the use of the improved specific gravity balance. Students of the College of the City of New York had several exhibits. Mr. M. C. Bates showed transparent hexagonite crystals from Balmat, N. Y., a most unusual specimen of this mineral.

A large map was prepared showing the principal mineral localities within a 50 mile radius of New York City, with specimens and explanatory labels to show where the specimens were collected.

F. H. POUGH, *Secretary*

*American Museum of Natural History, New York City, March 17, 1937*

With President B. T. Butler presiding, the meeting was called to order, 65 members and guests being present. The plans for a club field trip to Amelia, Virginia, were announced.

The speaker of the evening, Dr. Lester W. Strock, then spoke upon the "Spectrographic Analysis of Minerals." The discussion of the manner of making accurate quantitative analyses was clearly presented by means of slides illustrating the various steps in the work. He then showed the results of some of his work on the distribution of lithium in the rocks of the earth's crust, with an explanation of his unexpected discovery of its concentration in the monoclinic pyroxenes.

In conclusion some interesting slides were shown by Dr. Strock of a trip to Vesuvius and a descent into the first crater.

F. H. POUGH, *Secretary*

*American Museum of Natural History, New York City, April 21, 1937*

With President Butler presiding, the meeting was called to order, 85 members and guests being present. The annual election was held, with the incumbent officers unanimously re-elected for another term. The business meeting was followed by an address by Prof. B. M. Shaub, of Smith College, upon the "Photographing of Minerals in Color."

The first few slides were pictures of the equipment used by Prof. Shaub in his work showing the arrangement of the apparatus and the lights. Some ingenious and inexpensive pieces of accessory equipment which greatly facilitate the manipulation of the apparatus have been developed through experience. Results have shown that a slightly different technique from simple black and white photography is necessary.

For greater magnifications, Prof. Shaub has developed a long extension tube in which the lens is placed, and by its use enlargements up to 14 diameters on the plate may be secured. The lens is used at a small opening to give a maximum depth of focus. For the lower magnifications photoflood or 500 watt projection bulbs are used; for the others, small arc lamps with a water-cell interposed and a 50 mm. condensing lens are very satisfactory. Exposures range from 20 to 90 seconds. The most important, and the most difficult part of the entire process is selecting the correct exposure, especially in small objects where a photoelectric exposure meter cannot be used. Correct color rendition is secured only with proper exposure, for the plates have little latitude and many attempts are some-

times necessary. The Finlay plates, with their greater freedom in manipulation are more satisfactory in this respect than the Agfa. The Agfa, on the other hand, appear to give a better rendition of some colors, especially yellow. As the Agfa plates can only be duplicated by making a new photograph, they are less satisfactory, and on the whole, more expensive than the Finlay process. Both have advantages and disadvantages that make neither entirely preferable. Many slides of both makes were shown, covering all phases from hand specimens through moderate enlargements to photomicrographs of thin sections and interference figures. When the process has been developed so that there is greater certainty about exposures, and consequently, results, color photography should become an important tool of the mineralogist.

F. H. POUGH, *Secretary*

#### PHILADELPHIA MINERALOGICAL SOCIETY

##### *Academy of Natural Sciences of Philadelphia, January 7, 1937*

Mr. Arndt presided at a stated meeting with 43 members and 26 visitors present. The death of Alexander Fleming, Jr. on January 3 was announced.

Dr. Edgar T. Wherry gave a talk on "Recollections of Past Mineral Collecting Trips." Excursions were reported by Louis Moyd, Albert Jehle and William C. Knabe.

##### *Academy of Natural Sciences of Philadelphia, February 4, 1937*

Mr. Arndt presided with 46 members and 38 visitors present.

Dr. Alfred C. Hawkins spoke on "A Collecting Trip in Georgia" illustrated with lantern slides and many specimens obtained in the Stone Mountain region, and in the Birmingham, Ala., iron and coal mines. Mr. Charles R. Toothaker spoke on some interesting "Reminiscences of Brazil," describing visits to the gem districts of Minas Geraes and Goyaz. Mr. Edwin Roedder exhibited some synthetic "kongsbergite," "atacamite," and mercuric iodide crystals."

##### *Academy of Natural Science of Philadelphia, March 4, 1937*

Mr. Arndt presided with 101 persons present—53 members and 48 visitors.

Dr. Hugh E. McKinstry addressed the society on "Gold Mining in Eastern Australia." The talk was illustrated with lantern slides, charts, maps and specimens. The geology of some of the important fields and their commercial development were described.

W. H. FLACK, *Secretary*

#### MINERALOGICAL SOCIETY OF GREAT BRITAIN AND IRELAND

MINERALOGICAL SOCIETY, *March 11*, DR. L. J. SPENCER, President, in the chair.

DR. F. COLES PHILLIPS: *On a universal ore-polishing machine.*

A short account of the construction and use of a two-lap polishing machine available both for the usual methods of polishing by hand and for the automatic method developed at Harvard University. A description was given of the method of mounting specimens in synthetic material.

MR. ARTHUR RUSSELL: *On the occurrence of turquoise in Cornwall.*

A mineral assumed to be chrysocolla was collected from Bunny mine, Stenalees, St. Austell, many years ago when the mine was working. The best specimens came from the 80 fathom level in the main lode. In 1931 Mr. Herbert Thomas of Truro collected from the mine dump some of the same material which proved on chemical analysis to be turquoise. Another locality for turquoise has now been discovered at Castle an Dinas wolfram mine, St. Columb Major, Cornwall. It occurs in veins in tourmalinized slate with wolfram, scorodite, and wavellite.

MISS MARJORIE J. WHITEHOUSE (communicated by the President): *The deuteric mineral sequence in the Enoggera granite, Queensland.*

The minerals found in veins and vughs in this granite near Brisbane are described. The period of main magmatic consolidation was followed by pegmatite formation and the initiation of cavities in the rock. While the rock was still hot the deuteric period occurred beginning with the kaolinization of the feldspars and the chloritization of the ferromagnesian minerals. Then followed the deposition of chlorite and epidote, the pneumatolytic minerals, some calcite, the zeolites (prehnite, laumontite, gismondite) and, finally, many vughs were completely filled with calcite.

MR. M. PERUTZ (communicated by Prof. C. E. Tilley): *On iron-rhodonite, pyroxmangite, and their relations to rhodonite.* Determinations of the unit-cell of iron-rhodonite and approximate measurement of the dimensions of pyroxmangite have been made. The similarity of the structures of iron-rhodonite and pyroxmangite is established. By comparison with Gossner's description of rhodonite the conclusion is arrived at that the structure of the former minerals is different from that of rhodonite. After a determination of the density, volume, and mass of the cell of iron-rhodonite, possibilities of relations with enstatite were suggested.

## BOOK REVIEWS

DIE FEDOROW-METHODE. W. NIKITIN, University of Ljubljana. Published by Borntraeger, Berlin, 1936, 109 pp. 41 text figures. 7 plates. Price, RM. 12.40.

Professor Nikitin has long been recognized as an outstanding authority on the Fedorov method of use of the universal stage. This volume gives a concise account of the stage and its use, and includes additions of recent years to the technique.

Forty-five pages are given to a summary of the general description and manipulation of the stage, emphasizing the four axis stage with which Professor Nikitin has dealt in earlier publications. Special refinements are described for the study of minerals of low birefringence, and for the study of dispersion. The use of convergent light on the universal stage is also described as a means of attaining greater accuracy.

A leading contribution of the book is the description of a method of determining the refringence of a crystal by measuring the angle at which total reflection is obtained on balsam filled cleavages. No great accuracy is claimed for this procedure but even an approximation is a welcome contribution in the study of grain mounts especially.

The methods of Boldyrew, Berek and Dodge for determining the relationship between the optic axial angle and birefringence are given together with the diagrams which these men have published.

A detailed description is given of the method of learning the orientation relationship between the indicatrix and the crystallographic elements of a mineral. The application of these principles is made to the determination of twin laws.

The last section deals with the study of feldspars according to the methods of Fedorov.

R. C. EMMONS

ATLAS DER ANALYSEN-LINIEN DER WICHTIGSTEN ELEMENTE, FRITZ LÖWE, 37 pp., 3 figs. 16 full page plates. Dresden and Leipzig, Th. Steinkopf, 1936 (RM. 10.00).

This book is a second edition of the author's "Atlas der Letzten Linien" (published in 1928. Separate spectra of the following 46 elements are reproduced and arranged in alphabetical order. Ag, Al, As, Au, B,\* Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs,\* Cu, Fe, Ge,\* Hg, Ir, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Rb,\* Rh,\* Sb, Si, Sn, Sr, Ta, Te, Th, Ti, Tl,



U,\* V, W, Zn, Zr. Those marked (\*) were rephotographed for this edition. Facing these plates are wave length tables of the most important lines. The spectra for 17 elements are reproduced in two different spectral ranges. Two to four individual spectra of each element prepared by sparking varying weights of material are shown in juxtaposition, which is of great value in selecting useful lines for analytical work.

There are 9 pages of text which contains a brief annotated bibliography of published wave length tables and atlases. The wave lengths of 629 important lines are arranged in numerical order on the last ten pages of the book. The next (longer) stronger line is stated for each. This compact little volume can be recommended both as a handy laboratory manual and reference book of spectral line patterns, as well as a convenient wave length tabulation of the most characteristic spectral lines.

LESTER W. STROCK

**ELEMENTS OF OPTICAL MINERALOGY**—An Introduction to Microscopic Petrography. ALEXANDER N. WINCHELL. Fifth edition, revised and enlarged. *Part I. Principles and Methods*. xii+263 pages, over 300 illustrations. John Wiley & Sons, Inc., New York, 1937, Price \$3.50.

Professor Alexander N. Winchell's book on *Optical Mineralogy*, has served for many years as one of the leading American texts in this field of Mineralogy. Its popularity is shown by the short intervals between succeeding editions especially in recent years: 1908, 1922, 1928, 1931, 1937.

In this the fifth edition the changes made have been in the nature of corrections, minor additions and refinements. Over 60 new or revised illustrations have been added, including recent models of microscopes and other accessory optical instruments. The last chapter is devoted to "Special Methods of Study" in which the applications of the universal stage of Fedorov and the dispersion methods of immersion liquids for the accurate determination of the optical properties of crystallized materials are described in considerable detail.

W. F. H.

## NEW MINERAL NAMES

### Chlopinite (Klopinite, Hlopinite)

I. E. STARIK: Studies of the "lead method" for measuring geologic time and its application to the determination of chlopinite from Khilok, Transbaikalia. *Inter. Geol. Cong. Report of the XVI session*, U. S. A., 1933, vol. 1, pp. 217-224, 1936.

NAME: In honor of the Russian chemist, V. G. Chlopin.

CHEMICAL PROPERTIES: A columbo-titanate of uranium, thorium, yttrium and iron.  $M_2Cb_2TiO_9$ . Analysis:  $Cb_2O_5$  39.92,  $Ta_2O_5$  7.37,  $TiO_2$  10.01,  $SiO_2$  0.61,  $UO_2$  8.12,  $ThO_2$  2.22,  $Y_2O_3$  17.65,  $Fe_2O_3$  8.16,  $FeO$  1.83,  $MnO$  0.26,  $CaO$  0.96,  $PbO$  0.19,  $BeO$  0.03,  $K_2O+Na_2O$  0.24,  $H_2O$  2.94. Sum 100.64. 1.15 cc. helium per gram.

PHYSICAL PROPERTIES: Color black. Isotropic,  $n > 1.768$ .  $G = 5.24$ .

OCCURRENCE: Found with monazite and feldspar at Khilok, Transbaikalia.

W. F. FOSHAG

### Talasskite

W. D. NIKITIN: A new variety of the olivene group. *Mem. Soc. Russe. Mineral.*, 2d series, vol. 65, pp. 281-288, 1936.

NAME: From the locality, Talassa Valley, Kirghizian, U. S. S. R.

CHEMICAL PROPERTIES: A silicate of ferrous and ferric iron,  $(FeMg)_6 Fe'''(SiO_4)_3$ . Analysis:  $SiO_2$  29.87,  $TiO_2$  0.08,  $Fe_2O_3$  12.07,  $FeO$  54.88,  $CaO$  0.20,  $MgO$  2.54,  $Na_2O$  0.71,  $K_2O$  0.08,  $MnO$  0.02; Sum 100.45.



PHYSICAL AND OPTICAL PROPERTIES: Color brown, translucent. Not pleochroic. Biaxial.  $2V=49^\circ$ . Dispersion weak,  $r>v$ . Plane of the optic axes parallel to the (001) cleavage.  $X=b$ ,  $Y=c$ ,  $Z=a$ . Cleavage (001) and (010) perfect, (100) good. Brachydome cleavage poor. *G.* 4.1

OCCURRENCE: Found in masses of 4–5 cm. size in a pegmatite vein cutting alaskite granites in the Talassa Valley, Kirghizian, U. S. S. R.

W. F. F.

#### Labite

N. E. EFREMOV: Labite, a new mineral. *Mem. Soc. Russe Mineral.*, Ser. 2, 65, pp. 108–117, 1936. English summary.

NAME: From the locality Bolshaya Laba, Northern Caucasus.

CHEMICAL PROPERTIES: A hydrous silicate of magnesium.  $H_2MgSi_3O_8 \cdot H_2O$ . Analysis: (1)  $SiO_2$  66.23,  $Al_2O_3$  2.24,  $Fe_2O_3$  0.69,  $CaO$  1.15,  $MgO$  14.66,  $H_2O+7.04$ ,  $H_2O-8.39$ ; Sum 100.40. (2)  $SiO_2$  67.43,  $Al_2O_3$  1.83,  $Fe_2O_3$  0.50,  $CaO$  0.55,  $MgO$  15.61,  $H_2O+7.10$ ,  $H_2O-7.33$ ; Sum 100.35.

PHYSICAL AND OPTICAL PROPERTIES: Color yellowish green. Biaxial, negative;  $n$ =about 1.52, birefringence 0.004–0.006. Extinction parallel; plane of the optic axes parallel to the fibers. *G.* about 2.25.

OCCURRENCES: As an aggregate of interlaced fibers in serpentine near granite contact in Laba province, northern Caucasus.

W. F. F.

#### Calcium ferri-phosphate

N. E. EFREMOV: Calcium ferri-phosphate, a new mineral of the phosphate class. *Mem. Soc. Russe Mineral.*, Ser. 2, 65, pp. 225–232, 1936, with English summary.

CHEMICAL PROPERTIES: A hydrous phosphate of calcium and ferric iron.  $2CaO \cdot 3Fe_2O_3 \cdot P_2O_5 \cdot 10H_2O+$ . Analysis:  $P_2O_5$  22.70,  $CaO$  8.20,  $FeO$  0.53,  $MgO$  0.62,  $MnO$  0.12,  $Fe_2O_3$  28.96,  $Al_2O_3$  2.65,  $SiO_2$  1.42,  $H_2O+1.346$ ,  $H_2O-20.89$ ; Sum 99.55. Soluble in acids.

PHYSICAL AND OPTICAL PROPERTIES: Color light brown. Isotropic,  $n=1.605$ – $1.610$ . Hd. between 2 and 3. Brittle. Gel-like.

OCCURRENCE: Found in fossil shells in the iron ore beds of the Zelesny ravine, Tamanskaya, South Russia.

W. F. F.

#### Vanado-Magnetite

G. H. TEPPER: Vanadium-bearing magnetite deposits of Dhalbum and Mayurbhang, Behar, India. *Bull. Imp. Inst. London*, vol. 34, No. 4, pp. 449–452, 1936.

Analysis of magnetites found at Dublabera, Kumharoubi, and other localities in north-eastern India showed vanadic oxide contents ranging from 0.59% to 4.84%. Reference is made to vanado-magnetite, without further data, as a constituent of these magnetites, associated with magnetite, hematite, ilmenite and rutile.

W. F. F.

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#### PRESENTATION TO PROFESSOR CHARLES PALACHE

On May 24, at an informal meeting of the Division of Geological Sciences of Harvard University, a collection of "Studies in Mineralogy" was presented to Professor Charles Palache as a token of personal regard and an appreciation of his outstanding and still-continuing service to mineralogy. The presentation volume, which forms the May issue of

*The American Mineralogist*, contains thirty-five papers by American and European mineralogists and a list of Professor Palache's writings. The short speeches of congratulation emphasized Doctor Palache's eminence as investigator and teacher, collector and curator, and his constant encouragement to every form of mineralogical study. In reply Professor Palache expressed his total surprise at the appearance of the volume and his sincere appreciation of the tribute it conveyed.

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Dr. C. H. Smyth, Jr., emeritus Professor of Geology at Princeton University, died April 4 at the Princeton Hospital, from pneumonia and complications resulting from a fractured hip received in a fall two weeks previously. He was 71 years old. He was a member of the Hamilton College faculty for 14 years and of the Princeton faculty for 29 years. His major scientific contributions related to the Clinton type of iron ore, the regional geology and mineral deposits of the northwest Adirondacks, the origin of alkali-rich igneous rocks, and problems of chemical geology.

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Mr. Edgar H. Bailey of Ontario, California, has been appointed Teaching Fellow in Mineralogy at Stanford University for 1937-38.

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#### Correction

In the April issue of *The American Mineralogist* transpose the first two lines on page 269.